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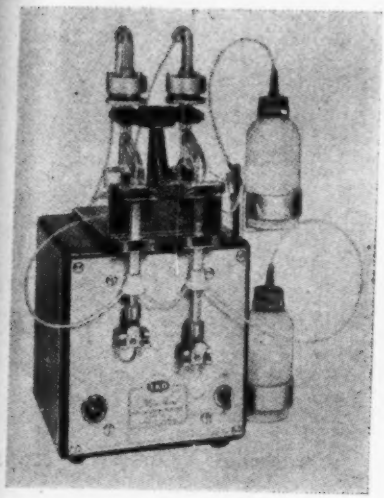

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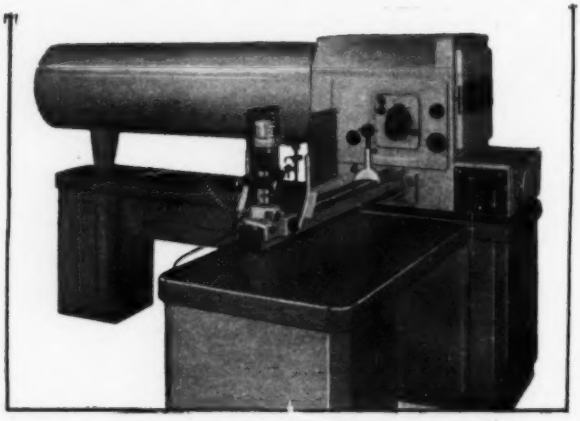

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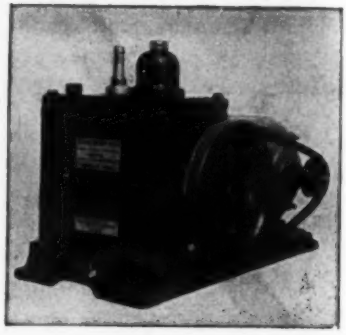

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[Jour. Indian Chem., Soc., Vol. 38, No. 12, 1961]

Isolation of Bound Ascorbic Acid (Ascorbigen) from Cabbage

M. C. Malakar and B. C. Guha

Bound ascorbic acid (ascorbigen) has been isolated from cabbage juice by adsorption on active charcoal and purification by chromatography on silica gel column with gradient elution. Ascorbigen shows reactions for ascorbic acid and an indole moiety.

It has already been reported that a certain amount of ascorbic acid is present in a bound form, called 'ascorbigen', in cabbage, cauliflower, and some other plant materials and that the substance can be extracted from cabbage (Guha *et al.*, *Nature*, 1936, **137**, 946; 1938, **141**, 974; Pal and Guha, this *Journal*, 1939, **16**, 481). Sengupta and Guha (this *Journal*, 1939, **16**, 496) and Ghosh and Guha (*ibid.*, 1939, **16**, 505) concentrated ascorbigen from cabbage to a considerable extent, but the substance was still gummy and obviously impure.

Recently Sumcov (*Biochimija*, 1950, **15**, 112), Terent'eva (*ibid.*, 1953, **18**, 296), and Procházka (*Chem. Listy*, 1953, **47**, 1643) took up this problem and Procházka *et al.* (*Coll. Czech. Chem. Comm.*, 1957, **22**, 654) claimed the isolation of ascorbigen from cabbage juice in a pure state and postulated a structure consisting of asocorbic acid and an indole moiety. The problem of isolation of ascorbigen was taken up in this laboratory again in 1956 and a preliminary communication was published elsewhere (Malakar and Guha, *Science & Culture*, 1958, **24**, 147).

The present communication deals with the method used in this laboratory for the isolation of what appears to be pure ascorbigen from cabbage. The preparation obtained is free from ascorbic acid as it does not reduce 2, 6-dichlorophenol indophenol. On hydrolysis, however, it releases ascorbic acid which has been identified both chromatographically and by the formation of 2,4-dinitrophenylhydrazone of dehydroascorbic acid derived from it. The substance shows reactions for indole. It closely resembles the substance obtained by Procházka *et al.* (*loc. cit.*) in appearance, composition, and properties and is probably identical with it.

EXPERIMENTAL

Cabbage (37 kg.), purchased from the local market, was washed and allowed to drain. It was cut into small pieces by a sharp stainless steel knife, repeatedly passed through a meat mincer, and the juice expressed by a screw press. The residue was mixed with about 8 litres of water, passed through the meat mincer twice, and pressed. The pressed juices were mixed (about 30 litres) and centrifuged in a Sharples supercentrifuge. The juice (*p*H 6.2) after centrifugation was taken in four aluminium buckets and active charcoal (25 g.) (E. Merck) was added in each bucket. After 4 hours' occasional stirring the liquid was

centrifuged and the charcoal pressed. The charcoal adsorbed about 70% of the bound ascorbic acid from the juice.

Various solvents, e.g., chloroform, ethyl acetate, 95% ethanol, 50% ethanol, and mixtures of chloroform and 95% ethanol (7:3 v/v and 3:7 v/v) were tried for elution of ascorbigen from charcoal. A mixture of chloroform and 95% ethanol (7:3, v/v) was found to be the best elutrient among these.

The charcoal was refluxed twice at 80° for one hour with a mixture of chloroform and 95% ethanol (7:3, v/v). About 35% ascorbigen was eluted by first extraction and another 15% by second extraction, totalling about 50%. A negligible amount was eluted by the third extraction. The extracts were mixed and concentrated by distillation under reduced pressure at 40° to a dark sticky mass. While cabbage juice contained about 0.5 mg. ascorbigen in terms of ascorbic acid per g. of total solid, this concentrate contained about 15-25 mg. ascorbigen per g. of total solid. The yield was about 28% of ascorbigen present in cabbage. The concentration effected was thus about 30 to 50 times. The concentrate (vacuum-dried) is soluble in water, ethanol, methanol, butanol^n, acetone, and ethyl acetate; it is less soluble in chloroform and practically insoluble in benzene and petroleum ether.

The vacuum-dried concentrate was dissolved in acetone, filtered, and added to an equal volume of petroleum ether (b.p. 60-80°). A dark red, oily liquid separated and this contained the major portion (about 95%) of ascorbigen. This oily substance had a specific activity* of about 50 mg./g. total solid and contained about 25% of ascorbigen present in cabbage.

Attempts were made to further purify this red liquid. It was dried in vacuum and chromatographic separation was attempted on cellulose (Schleicher and Schüll, Nr 123) column (1 cm × 15 cm; 3g.). The following solvents were tried as irrigating liquids: water-saturated ethyl acetate, water-saturated butyl^n acetate, water-saturated butanol^n, water-saturated phenol, butanol^n: acetic acid: water (4:1:5, v/v), butanol^n : petroleum ether (4:6, v/v.). Of these, water-saturated butyl^n acetate seemed to be the best, giving a fraction having a specific activity of 100 mg./g. total solid. This fraction contained about 15% of ascorbigen present in cabbage. On rechromatography, specific activity up to 130 mg./g. total solid could be obtained, but there was a loss of about 50% in yield. No further purification could be obtained on cellulose column.

As the partitioning power of cellulose for ascorbigen and impurities seemed to be low, attempts were made to fractionate the material on a silica gel (E. Merck, 0.2-0.5 mm for column chromatography) column (17 cm × 1.2 cm; 15g.). By using ethyl acetate and chloroform in the ratio of 1:1 (v/v) as the irrigating liquid, a fraction was obtained having a specific activity of 230 mg./g. total solid. Only 6.8 mg. out of 16 mg. (sp. activity 50 mg./g.) taken for chromatography was present in this fraction. This fraction containing about 10% of ascorbigen present in cabbage was rechromatographed and one fraction probably contained pure ascorbigen, as its specific activity (about 500 mg./g.) did not change on further chromatography. But the yield was very poor (only 0.4 mg. out of 6.8 mg.). This fraction contained only about 0.6% of ascorbigen present in cabbage. As the procedure was very time-consuming and required a large volume of irrigating liquid, stage chromatography was abandoned in favour of chromatography with gradient elution. To facilitate the rate

*Specific activity—mg. of ascorbigen (in terms of ascorbic acid) per g. of total solid.

of progress, an apparatus was made containing five silica gel columns with one reservoir and one mixing vessel (Fig. 1).

In this method ethyl acetate was kept in a separating funnel (500 c.c.) at a high level and with the help of adjustable narrow glass tubes it was allowed to fall dropwise into a lower vessel (1 litre) containing chloroform. This vessel was provided with side tubes (with stop cocks) to which were fitted the silica gel columns (14 cm × 1.5 cm; 15 g.). Into each column, about 0.25 g. of ascorbigen (sp. activity 50 mg./g.) was introduced. All the connections were of ground-glass fittings. The contents of the vessel were stirred continuously with the help of a magnetic stirrer. The apparatus was so regulated that the rate of outflow from the silica gel columns was equal to that of inflow into the vessel from the separating funnel above. Fractions (25 c.c.) were collected at intervals of about 30 minutes.

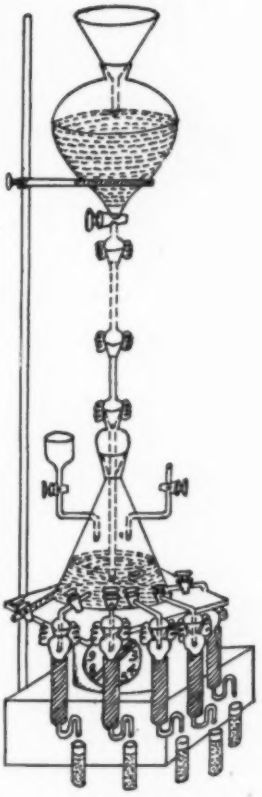

FIG. 1

The active substance began to appear in the 7th fraction and was present in maximum amount in the 9th fraction. The concentration then began to decrease gradually and the substance practically disappeared in the 12th fraction. The fraction having the highest amount contained 30% of the original amount taken for chromatography and the specific activity was about 230 mg./g. total solid. This fraction containing about 8% of ascorbigen present in cabbage was rechromatographed and this yielded a product which on further chromatography did not increase in specific activity (about 500 mg./g.). Yield was about one tenth of the amount originally taken for chromatography and contained about 2.5% of ascorbigen present in cabbage.

Properties of Ascorbigen.—Ascorbigen is a faintly yellowish powder, m.p. 84°. It is amorphous. Attempts to crystallise it were unsuccessful. It is highly hygroscopic and photosensitive, becoming brown to reddish on exposure to light. It is labile to acid and alkali. It shows reaction for indole with Ehrlich's reagent. It does not respond to the test for ascorbic acid unless hydrolysed with acid. It is dialysable.

Chromatographic Identification of Ascorbic Acid as a Moiety of Ascorbigen

Indophenol-reducing substance could not be detected in ascorbigen unless it was hydrolysed with acid. Spots of (*a*) ascorbigen, (*b*) hydrolysed ascorbigen, (*c*) pure ascorbic acid, and (*d*) hydrolysed ascorbigen plus pure ascorbic acid were given on Whatman paper No. 1. By ascending chromatography in a solvent mixture of butanol[n]: acetic acid: water (4:1:5) with a drop of 10% KCN (to keep ascorbic acid in reduced condition), spots with the same R_f (0.48) were detected on spraying with 2,6-dichlorophenol indophenol in all cases except in that of ascorbigen. Spots with the same R_f (0.75) were also detected

on spraying with the indophenol dye on Whatman paper No. 1 using a solvent mixture of methanol : butanol^n (4 :1, v/v) in all cases except in that of ascorbigen. This shows that ascorbigen on hydrolysis produces ascorbic acid which can be identified chromatographically.

Further Identification of Ascorbic Acid formed from Ascorbigen

The 2,4-dinitrophenylhydrazone derivative of dehydroascorbic acid, formed from ascorbic acid released by hydrolysis of ascorbigen, was prepared. Ascorbigen was dissolved in 5% metaphosphoric acid, heated on a boiling water bath in CO_2 atmosphere for 30 minutes, cooled, and filtered. Saturated bromine water was added to the filtrate in excess. Thiourea (2%) in 50% ethanol was added till the colour disappeared; 1 c.c. was added in excess. 2,4-Dinitrophenylhydrazine (50 c.c.) in 9*N*-H_2SO_4 was added to this solution and incubated at 37° for 6 days. The precipitated hydrazone derivative was filtered, washed with water, dissolved in methanol, and reprecipitated by the addition of water. The process was repeated several times. The precipitate was dissolved in 50% ice-cold H_2SO_4 and precipitated by careful addition of water. It was filtered, washed with water, and dissolved in absolute acetone. The volume was reduced by warming, cooled, and the hydrazone derivative allowed to crystallise; m.p. 272°. The 2,4-dinitrophenylhydrazone derivative from pure ascorbic acid was similarly prepared and purified; m.p. 271° (mixed m.p. 272°). This provides further evidence that ascorbigen contains ascorbic acid in a bound form.

Composition.—The elemental composition of ascorbigen is C, 58.78; H, 4.66; N, 3.72%. Procházka and Šanda (*Coll. Czech. Chem. Comm.*, 1960, **25**, 270) have given the elemental composition of their product as C, 58.74; H, 5.64; N, 4.36%.

Absorption spectra.—The absorption maxima and minima (with extinction coefficients) of ascorbigen are: λ_{max} 220 mμ (ϵ 4.52), 273 mμ (ϵ 3.77), 280 mμ (ϵ 3.79), 290 mμ (ϵ 3.73); λ_{min} 256 mμ (ϵ 3.59), 276 mμ (ϵ 3.77), 287 mμ (ϵ 3.69), whereas the corresponding data of Procházka's substance are: λ_{max} 220 mμ (ϵ 4.52), 273 mμ (ϵ 3.77), 280 mμ (ϵ 3.80), 290 mμ (ϵ 3.71); λ_{min} 245 mμ (ϵ 3.30), 276 mμ (ϵ 3.75), 287 mμ (ϵ 3.66).

Electrophoretic Studies.—Paper ionophoresis in phosphate buffer solution at *p*H 6.0 and 4.4 (ionic strength 0.05, voltage 220, milliamp 11, time 16 hours, temperature 4° ± 1°) indicates that ascorbigen is electroneutral at these hydrogen-ion concentrations.

Attempts to prepare some derivatives of the substance have so far been unsuccessful owing to the very small amount of material available and its great lability to acid and alkali.

Thanks of the authors are due to the Indian Council of Medical Research for a research grant.

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Received May 12, 1961

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Interaction of Charcoal and Bromine in Aqueous Solution

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The nature of the reaction between charcoal and bromine in aqueous solution depends to a large extent on the nature of the charcoal surface as influenced by its associated oxygen. When oxygen, capable of evolving carbon dioxide on high-temperature evacuation, is present, the reaction involves hydrolysis of bromine and chemisorption of an equivalent amount of oxygen. When this form of oxygen is absent, the reaction involves 'fixation' of an appreciable amount of bromine, probably at some unsaturated sites, there being little or no hydrolysis. The amount of bromine fixed is seen to be a definite quantity for a given sample of charcoal. The heat evolved during the process is quite close to the heat of addition of bromine in ethylenic double bond as reported in literature.

It appears from the literature that although the interaction of charcoal and carbon blacks with chlorine as well as iodine in aqueous solution has been studied by several workers (Behrman and Gustafson, *Ind. Eng. Chem.*, 1935, **27**, 426; Watson and Parkinson, *ibid.*, 1955, **47**, 1053; Smith *et al.*, 1941, **33**, 1303; Puri *et al.*, this *Journal*, 1960, **37**, 171, 401; Razouk and Shimmi, *A'in. Sham. Sci. Bull.*, 1957, No. 2, 203; King, *J. Chem. Soc.*, 1937, 489) and different mechanisms of the processes involved have been suggested, the interaction with bromine under similar conditions has not received as much attention. The present work was therefore undertaken.

EXPERIMENTAL

Two samples of charcoal, prepared by carbonisation of recrystallised cane sugar (by pure sulphuric acid followed by exhaustive washings with hot distilled water) and coconut shell charcoal (by burning small pieces at 350° in a limited supply of air), were used in these investigations. Sugar charcoal was almost free of ash; the other sample was extracted with hydrofluoric acid to lower the ash content to about 0.2%. These samples, referred to as 'original samples' in the text, were used as such as well as after evacuating at 750° and 1100°. The amount of combined oxygen as well as its disposition in each sample was estimated by evacuating 2 g. portion at 1200° in a resistance tube furnace, collecting water in calcium chloride tubes, and analysing the rest of the gases evolved in an Orsat-Lunge gas analysis apparatus in the usual way. The results are shown in Table I. It is seen that the original samples contain considerable amounts of chemisorbed oxygen which is evolved as carbon dioxide, carbon monoxide, and water. The samples degassed at 750° contain oxygen capable of evolving carbon monoxide and water only, but those degassed at 1100° do not contain any oxygen at all.

Aqueous solutions of bromine in potassium bromide of concentrations varying from 0.025 to 0.130*N* were used.

Procedure.—One g. portions of charcoal were mixed with 250 c.c. of bromine solution. The suspensions were shaken mechanically in half-pound stoppered bottles, wrapped in thick black papers, for different intervals of time, after which an aliquot of the supernatant liquid was examined for unchanged bromine and hydrobromic acid formed, if any, by the usual analytical methods.

Thermal Effect.—The heat evolved during the interaction of 750°- and 1100°-evacuated sugar charcoal with bromine water was determined by the calorimetric technique described earlier (Puri *et al.*, *J. Phys. Chem.*, 1958, **62**, 756). The charcoal sample (5 g.), suspended in CO_2-free water (25 c.c.) to eliminate immersional thermal effects, was immersed in bromine water (200 c.c.) of increasing concentration, contained in the calorimeter, with all necessary precautions. The rise in temperature was noted in the usual way after every 2 minutes till the rate of further rise of temperature became extremely slow. This usually required a little more than an hour. The charcoal was then taken out, washed exhaustively with water, and the solution analysed for its bromine content.

TABLE I

Combined oxygen evolved as oxides of carbon and water on evacuating different samples of sugar and coconut shell charcoals at 1200°.

Description of the sample.	Oxygen (g./100 g.) evolved as CO_2.	CO.	H_2O.	Total combined oxygen (g./100 g.).
		Sugar charcoal.		
Original	10.77	8.05	11.11	29.93
Degassed at 750°	Nil	5.54	5.73	11.27
Degassed at 1100°	Nil	Nil	Nil	Nil
		Coconut shell charcoal.		
Original	5.07	6.22	6.86	18.15
Degassed at 750°	Nil	4.34	5.38	9.72
Degassed at 1100°	Nil	Nil	Nil	Nil

TABLE II

Interaction of the original samples of sugar and coconut shell charcoals with bromine water.
Amount of bromine added to 1 g. charcoal=250 c.c. of 0.075*N* (18.75 m.e.).

Time of shaking.	Analysis of bromine water (in m.e.) after shaking for different intervals of time. Bromine unchanged.	HBr formed.	Total amount of Br_2 and HBr.	%Bromine converted to HBr.	Bromine unchanged.	HBr formed.	Total amount of Br_2 and HBr.	%Bromine converted to HBr.
	Sugar charcoal (original).				Coconut shell charcoal (original).			
2 hrs.	14.29	4.46	18.75	23.78	16.16	2.56	18.72	13.65
4	12.95	5.80	18.75	30.93	15.11	3.62	18.73	19.30
6	11.40	7.30	18.70	38.93	14.53	4.19	18.72	22.35
8	9.78	8.87	18.65	47.31	12.80	5.86	18.66	31.25
12	8.92	9.72	18.64	51.84	12.52	6.18	18.70	32.96
24	7.20	11.40	18.60	60.80	11.47	7.24	18.71	38.61
48	7.03	11.52	18.55	61.44	11.09	7.54	18.63	40.21
120	6.99	11.59	18.58	61.81	11.05	7.60	18.65	40.53

TABLE III

Account of oxygen rendered available (in m.e./g.) during the hydrolysis of bromine in presence of charcoal.

Description of the sample. (1)	Oxygen as free CO_2 formed during the reaction (2)	Oxygen evolved as CO_2. (3)	as CO. (4)	as H_2O. (5)	Total chemisorbed oxygen. (6)	Oxygen chemisorbed during the reaction with bromine. (7)	Total oxygen that can be accounted for (2+7). (8)	Amount of oxygen expected (equivalent to the amount of HBr produced). (9)
		Before treatment with bromine.						
Sugar charcoal		13.46	10.06	13.89	37.41	47.02-37.41 =9.61		
		After treatment with bromine.						
	2.06	23.12	9.98	13.92	47.02		11.67	11.82
		Before treatment with bromine.						
Coconut shell charcoal		6.34	7.78	8.58	22.70	28.92-22.70 =6.22		
		After treatment with bromine.						
	1.32	12.62	7.69	8.61	28.92		7.54	7.63

TABLE IV

Interaction of bromine water and evacuated samples of sugar charcoal.

Conc. of bromine water.	Bromine added to 1 g. charcoal (250×N).	Analysis of bromine water (in m.e.) after shaking. Evacuated at 750°. Bromine unchanged.	HBr formed.	Total amount of Br_2 and HBr (3+4).	Bromine 'fixed' by charcoal (2 to 5).	Evacuated at 1100°. Bromine unchanged.	HBr formed.	Total amount of Br_2 and HBr.	Bromine 'fixed' by charcoal.
(1)	(2)	(3)	(4)	(5)	(6)				
0.035 N	8.75 m.e.	4.00	0.25	4.25	4.50	3.90	0.20	4.10	4.65
0.055	13.75	8.82	0.28	9.10	4.65	8.80	0.20	9.00	4.75
0.075	18.75	13.90	0.30	14.20	4.55	14.05	0.20	14.25	4.50
0.095	23.75	18.85	0.30	19.15	4.60	18.98	0.22	19.20	4.55
0.115	28.75	23.76	0.26	24.02	4.73	23.91	0.24	24.15	4.60
0.130	32.50	27.52	0.30	27.82	4.68	27.72	0.25	27.97	4.53

TABLE V

Heat of 'fixation' of bromine by the 750°- *and* 1100°- *evacuated samples of sugar charcoal.*

Conc. of bromine soln.	Amount of bromine added (200×N).	Heat evolved during the fixation of bromine by charcoal.	Amount of bromine fixed by charcoal.	Heat of fixation of bromine (Kcal./mole).
		750°-evacuated sample.		
0.024N	4.8 m.e.	84.99 cal.	8.18 m.e.	20.78
0.038	7.6	139.65	14.57	19.17
0.063	12.6	170.64	16.40	20.81
0.151	30.2	190.82	18.64	20.47
		1100°-evacuated sample.		
0.026	5.2	8.08	7.98	20.07
0.054	10.8	100.75	10.25	19.66
0.093	18.6	132.27	13.12	20.16
0.112	22.4	172.28	16.55	20.82

DISCUSSION

It is seen (Table II) that there is a slow, though progressive, conversion of bromine into hydrobromic acid in presence of the original samples of sugar as well as coconut shell charcoals up to about 24 hours, after which a state of equilibrium appears to set in. The percentage conversion at any time is more in sugar charcoal than in coconut shell charcoal. This may be due to larger surface area of the sugar charcoal (Puri and Sharma, *J. Sci. Ind. Res.*, 1956, **15B**, 178). The hydrobromic acid formed was mostly in solution; only a small amount was found to be adsorbed by the charcoal, which too could be recovered on washing with hot distilled water. The values recorded in Table II represent the total amounts of the acid formed. The results of blank experiments (without charcoal) under similar conditions showed neither any formation of hydrobromic acid nor any decrease in the concentration of bromine.

The conversion of bromine into hydrobromic acid, as reported in Table II, is presumably due to hydrolysis of the halogen brought about in the presence of charcoal. An equivalent amount of oxygen therefore must be taken up by the charcoal in some form. In order to verify this, the gaseous mixture above the reaction bottle as well as that evolved on degassing the treated charcoals at 1200° was analysed by an Orsat-Lunge gas analysis apparatus in the usual way. The results are recorded in Table III. The amount of the gases evolved on degassing the same charcoals before treatment with bromine water, expressed in the same units, are also included for comparison. A considerable amount of oxygen, rendered available during the reaction with bromine water, appears to be chemisorbed by the charcoal (col. 7) and it is evolved mostly as carbon dioxide (col. 3) on high-temperature evacuation. A much smaller amount of the oxygen gives rise to gaseous carbon dioxide (col. 2) which collects in the reaction vessel. The total oxygen that can be accounted for in these two forms (col. 8) is almost exactly equivalent to the amount of hydrobromic acid formed (col. 9).

This agreement confirms the view that bromine is hydrolysed in presence of charcoal. Further, as the entire amount of bromine added can be accounted for as hydrobromic acid formed and as bromine left unchanged (Table II), it is evident that none of it is taken up as such by these samples of charcoal.

The results obtained on shaking with bromine solutions of varying concentrations with 750°-and 1100°- degassed samples of sugar charcoal for 24 hours are recorded in Table IV. There is little or no formation of hydrobromic acid now. An appreciable fall in the concentration of bromine was, however, noticed in each case. Similar results were obtained with the degassed coconut shell charcoals. Evidently degassed charcoals, devoid of chemisorbed oxygen disposed as carbon dioxide (Table I), unlike the original samples, can 'fix' an appreciable amount of bromine. This bromine could not be recovered on repeated washings with water nor even on high-temperature evacuation of the charcoal at 1200°.

Incidentally, the amount of bromine fixed by 750°- as well as 1100°-degassed sugar charcoal is about the same and almost independent of the initial concentration of the bromine solution. The average value is approximately 4.61 m.e./g. sugar charcoal. The corresponding value for degassed coconut shell charcoals is 3.75 m.e./g. These are appreciably high values and amount to 36.88% and 30.0% on the weight of these charcoals respectively. The results of ultimate analysis of the treated charcoals gave almost identical values.

This large amount of bromine is very likely linked to some unsaturated sites created by the elimination of that part of chemisorbed oxygen which is evolved as carbon dioxide. The elimination of the rest of the oxygen, evolved as carbon monoxide and water, does not appear to cause any additional unsaturated sites because, although the 750°- and 1100°-evacuated samples differ appreciably in their oxygen of this form (Table I), there is no noticeable difference in the amounts of bromine 'fixed' by them. Such unsaturated sites are apparently absent in the original samples since these are incapable of 'fixing' any bromine. These can bring about, however, hydrolysis of bromine to a considerable extent, as already shown (Table II). Thus the nature of the reaction between charcoal and bromine in aqueous solution depends very largely on the nature of the charcoal surface.

The results of thermal measurements using bromine solutions of different concentrations with 750°- and 1100°- degassed charcoals are recorded in Table V. Contrary to the results reported in Table IV, the amount of bromine 'fixed' by charcoal is now seen to increase with the initial concentration of the solution and the cause is attributed to the duration of these experiments for one hour only. Whenever sufficient time was allowed for the attainment of the equilibrium, the amount of bromine 'fixed' was invariably about the same and independent of the concentration of the bromine solution used.

It is noteworthy that the heat of 'fixation' of bromine per mole is almost the same in each sample of charcoal, irrespective of the concentration of the solution used or of the amount of the reactants. The average value is seen to be about 20.24 Kcal./mole.

The heat of addition of bromine in ethylenic double bond has been found to be between 28 and 31 Kcal./mole (Lister, *J. Amer. Chem. Soc.*, 1941, **63**, 143; Mochulsky and Tobolsky, *Ind. Eng. Chem.*, 1948, **40**, 2155). This heat refers to the reaction of bromine in the gaseous phase. By adding heat of condensation of bromine (7.50 Kcal./mole) and its heat of solution in potassium bromide (3.7 Kcal./mole, as determined by the authors in the concentration range used by them) to 20.24 K.cal., a value equal to 31.44 Kcal. is obtained, which is quite close to the value reported in literature. This agreement indicates that the bromine 'fixed' by degassed charcoal is taken up at some unsaturated sites.

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Received June 17, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Properties of Mixtures of Clay Minerals. Part II. Ternary Mixtures

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Studies have been made on the differential thermal analysis and on the variations in the *p*H, specific conductance, cationic activity, and viscosity on the progressive addition of bases to six ternary mixtures of kaolinite, montmorillonite, and illite. An examination of the total acidities and *p*H at inflection in the *p*H-base concentration curves, total acidity at the breaks of the conductometric titration curves, cationic dissociation, variation of viscosity on the addition of bases to H-clay mixtures, and the differential thermal analysis data indicates that individual constituents markedly influence the properties of other constituents in the mixture and the conclusion drawn from any single measurement is likely to lead to erroneous results. Attempts have been made to establish certain criteria for identification and estimation of individual clay mineral constituents in the mixtures.

As reported in Part I (this *Journal*, 1961, **38**, 725), identification of individual components present in binary mixtures of clay minerals requires careful consideration of several aspects of the (*i*) potentiometric and conductometric titration curves of the H-systems with bases, (*ii*) D.T.A. curves, and (*iii*) variations in the viscosity of the H-systems with the progressive addition of bases. It has also been observed that conclusions drawn on the basis of any single measurement may often lead to erroneous results. The soils usually contain mixtures of three common clay minerals, viz., kaolinite, montmorillonite, and illite. With a view to establishing criteria which might be used for the identification and estimation of individual clay minerals commonly present in soils, ternary mixtures of varying composition of kaolinite, illite, and montmorillonite have been subjected to differential thermal analysis and conductometric, potentiometric, and viscometric masurements. The different ternary mixtures used in the present study have the following compositions (proportions by weight on oven-dry basis):

TABLE A

	Kaolinite.		Illite.		Montomorillonite.
(*a*)	40%	+	20%	+	40%
(*b*)	80	+	10	+	10
(*c*)	10	+	30	+	60
(*d*)	40	+	40	+	20
(*e*)	10	+	10	+	80
(*f*)	10	+	80	+	10

The details of experimental procedures adopted were reported in Part I (Sarkar and Chatterjee, *loc. cit.*).

DISCUSSION

The D. T. A. diagrams of ternary mixtures, shown in Fig. 1, indicate that the endothermic peak near the region of 700° due to the presence of montmorillonite in the mixtures observed in all the mixtures with the exception of the ternary mixtures containing 10% montmorillonite. The individual endothermic peaks of kaolinite and illite in the zone of 500-600° could not be observed, but instead a single common endothermic peak was noticed. In this connection it will not be out of place to mention that according to Grim (*Am. Min.*, 1947, **32**, 493), the thermal reactions of individual component of the mixtures are not always discernible, particularly if the mixing is very intimate and if the components are

poorly crystallised. The single exothermic peak for the ternary mixtures observed between 940° and 970° seems to indicate that kaolinite in the mixture exerts a greater influence on the position of the exothermic peak temperature and also on the size and sharpness of the resulting graph. This observation is true even when 10% kaolinite is present in the ternary mixture. The endothermic peak between 100° and 200° due to illite and montmorillonite is observed even in the mixture containing 10% illite, 10% montmorillonite, and 80% kaolinite.

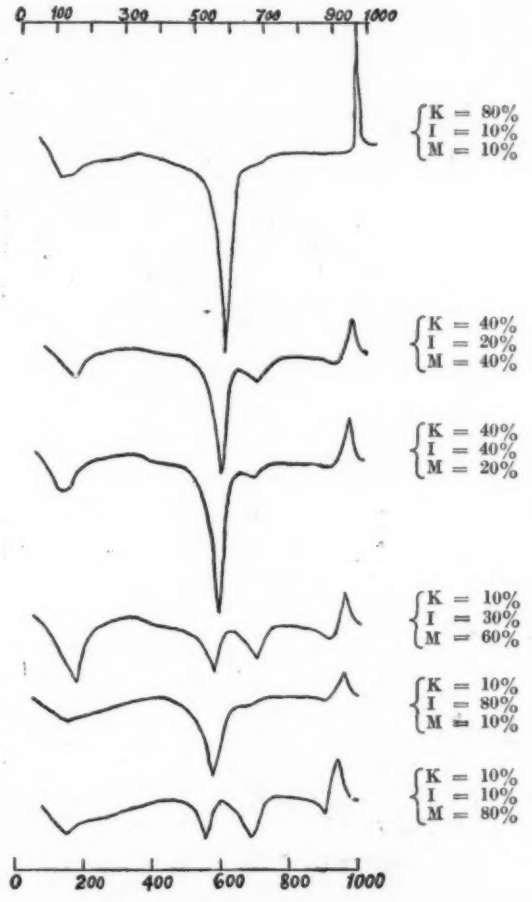


FIG. 1. D.T.A of ternary mixture of clay minerals.
K, I, and M denote respectively kaolinite, illite and montmorillonite.

Potentiometric and Conductometric Titration Curves

The potentiometric and conductometric titration curves of ternary mixtures have been shown in Figs. 2-7 and the results have been presented in Table I. The potentiometric titration curves of ternary mixtures of kaolinite, illite, and montmorillonite show two inflec-

tion points—one in the region of *p*H 6.5—8.2 and the other between *p*H 10.1 and 10.8. Another inflection point at *p*H 8.4 has been observed only in the case of titration with KOH of a mixture containing 80% kaolinite, 10% illite, and 10% montmorillonite. The high total

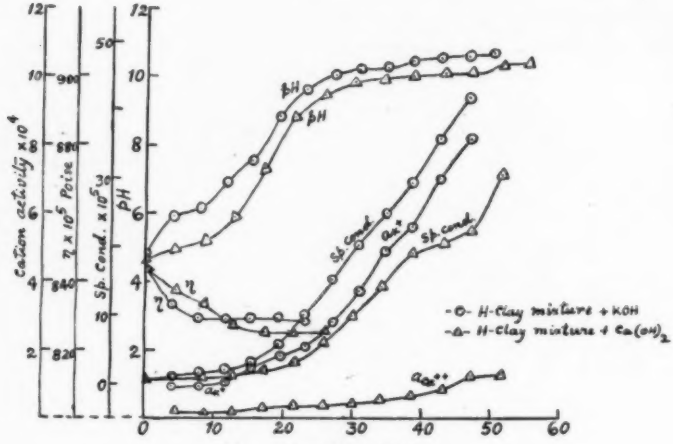


FIG. 2. A mixture of 80% K+10% I+10% M.

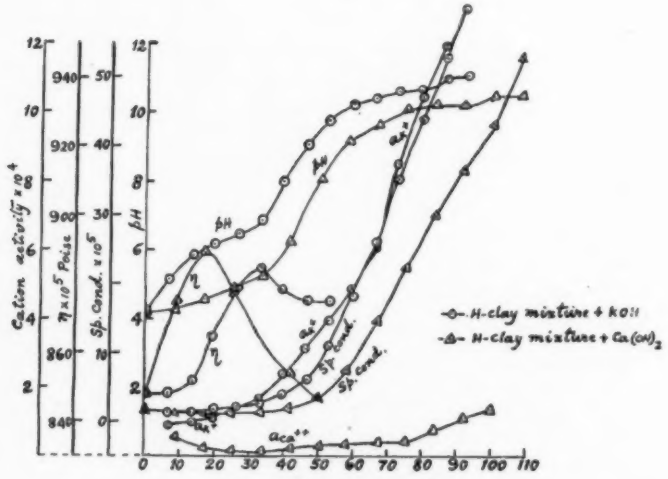


FIG. 3. A mixture of 40% K+20% I+40% M.

acidity observed at the second inflection point between *p*H 10.1 and 10.8 may probably be attributed to the considerable buffer action of H-montmorillonite in this *p*H region. Thus, the third inflection point around *p*H 10.4 observed (Mitra and Rajagopalan, *Nature*, 1948, **162**, 104) in the potentiometric titration curve of H-illite with bases is found only when an extra amount of base is added to overcome the buffer action due to the presence

of montmorillonite. It has been observed (Table II) that with one or two exceptions, the total acidity values observed at the first inflection point of the ternary mixtures are in general agreement with the calculated ones, based on the total acidities of kaolinite and illite at the second inflection point and that of montmorillonite at the first inflection point. The total acidity value observed at the second inflection point of the ternary mixture is found to be much greater than that calculated based on the total acidity of kaolinite at the second inflection point, that of illite at the third inflection point, and of

TABLE I

Total acidity of ternary mixture of clay minerals.

Samples.	Base used.	Total acid (m.e. per 100 g. of clay). Potentiometric curves. 1st inflec.	2nd inflec.	3rd inflec.	Conductometric curves. 1st break.	2nd break.
1. H-kaolinite 80% + H-illite	KOH	10.0(6.5)*	18.0(8.4)	36.5(10.3)	17.0	38.0
10%+ H-montmorillonite 10%	$Ca(OH)_2$	18.0(7.7)	50.0(10.2)	-	20.0	47.5
2. H-kaolinite 40% + H-illite	KOH	38.0(7.6)	84.0(10.8)	-	44.0	80.0
20%+H-montmorillonite 40%	$Ca(OH)_2$	45.0(7.1)	97.0(10.3)	-	51.0	100.0
3. H-kaolinite 40% + H-illite	KOH	27.5(8.2)	49.0(10.2)	-	28.0	42.5
40% + H-montmorillonite 20%	$Ca(OH)_2$	35.0(7.9)	62.0(10.1)	-	36.0	64.0
4. H-Kaolinite 10% + H-illite	KOH	57.0(7.7)	102.0(10.4)	-	58.0	100.0
30%+ H-montmorillonite 60%	$Ca(OH)_2$	65.0(7.2)	128.0(10.2)	-	70.0	112.0
5. H-kaolinite 10% + H-illite		57.0(7.5)	130.0(10.6)	-		
10% + H-montmorillonite 80%	KOH					
6. H-kaolinite 10% + H-illite	KOH	22.0(7.5)	58.0(10.5)	-		
80% + H-montmorillonite 10%						

*Figures within parenthesis denote *p*H at inflection.

TABLE II

Observed and calculated total acidities of ternary mixtures of clay minerals.

System.	Base used.	Total acidity at 1st inflec. (m.e. per 100g.) Obs.	Calc.	Total acidity at *p*H 7.0. (m.e./100g.) Obs.	Calc.	Total acidity at 2nd inflec. (m.e./100g.) Obs.	Calc.
1. H-kaolinite 80% + H-illite 10%	KOH	10.0	20.0	12.0	15.9	18.0	23.2
+H-montmorillonite 10%	$Ca(OH)_2$	18.0	21.0	16.5	14.5	50.0	25.8
2. H-kaolinite 40% + H-illite 20%	KOH	38.0	41.6	35.0	34.2	84.0	48.1
+H-montmorillonite 40%	$Ca(OH)_2$	45.0	46.0	45.0	39.2	97.0	54.5
3. H-kaolinite 40% + H-illite 40%	KOH	27.5	33.8	21.5	25.6	49.0	46.7
+H-montmorillonite 20%	$Ca(OH)_2$	35.0	38.4	30.0	27.8	62.0	55.3
4. H-kaolinite 10% + H-illite 30%	KOH	57.0	55.9	50.0	46.8	102.0	66.5
+H-montmorillonite 60%	$Ca(OH)_2$	65.0	63.5	64.0	56.3	128.0	76.1
5. H-kaolinite 10% + H-illite 10% +H-montmorillonite 80%	KOH	57.0	64.7	54.0	55.8	130.0	67.9
6. H-kaolinite 10% + H-illite 80% +H-montmorillonite 10%	KOH	22.0	37.0	20.0	24.3	58.0	63.0

montmorillonite at the first inflection point. This discrepancy seems to arise on account of the great buffering action of H-montmorillonite in this *p*H region. The results obtained indicate that the five inflection points, viz., two for kaolinite, first two for illite, and one for montmorillonite, have probably merged into one and that the third inflection point, characteristic of illite, corresponds owing to the buffering action of H-montmorillonite to a higher total acidity (Mukherjee and Mitra, *J. Colloid Sci.*, 1946, **1**, 141; Mitra and Rajagopalan, *loc. cit.*; Sarkar and Chatterjee, *loc. cit.*).

Conductometric titration curves of ternary mixtures show two breaks corresponding to the inflections in the potentiometric titration curves. In case of the mixture containing 80% kaolinite, 10% illite, and 10% montmorillonite, the conductometric titration curve with KOH shows only two breaks, whereas the corresponding potentiometric titration curve shows three inflection points. The total acidities corresponding to the first and the second breaks of the former are more or less the same as those obtained from the second and third inflection points of the latter.

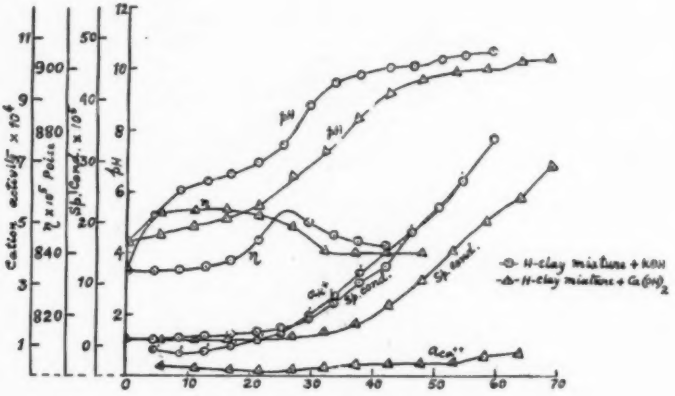
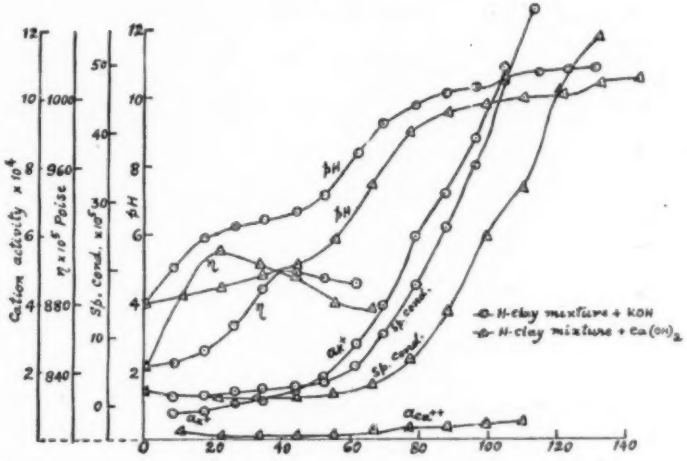


FIG. 4. A mixture of 40% K+40% I+20%M.

Viscometric Titrations of Ternary Mixtures of Clay Minerals

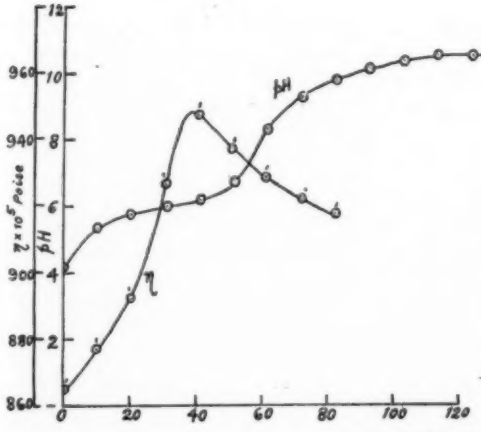
In the ternary mixtures (*a*), (*c*), (*d*), and (*f*) (Table A), the viscosity-KOH neutralisation curves (Figs. 3-5,7) show that viscosity initially remains unaffected with gradual addition of KOH up to about 20% neutralisation, then it rises to a maximum at about 70% neutralisation, and finally falls. The initial feature of the curve seems to be due to kaolinite (Mukherjee and Mitra, *loc. cit.*) in the ternary mixtures and this is noticed even when 10% kaolinite is present (Figs. 5 and 7) except in the mixture (*e*) (Table A) which contains a large percentage of montmorillonite. In this case a gradual increase in viscosity is observed on the addition of KOH, which rises to a maximum at about 70% neutralisation (Fig. 6). The maximum viscosity observed in the viscosity-KOH curve of illite around 30-40% neutralisation is absent with all the ternary mixtures studied. The curve of the mixture (*b*) (Fig. 2) shows only the characteristics of kaolinite, *i.e.*, a gradual fall in viscosity attaining finally a constant value. The viscosity data thus indicate that the presence of kaolinite or montmorillonite in large amounts (80% or so) masks the presence of the other

two in a ternary mixture, but in other cases, the viscosity—base concentration curves give an idea of the different clay minerals present in the mixture; the initial portions of the viscosity—base concentration curves of H-clays give an indication of the presence or otherwise of kaolinite in the mixture.



M. e. of base/100 *g. of* H-*clay.*

FIG. 5. A mixture of 10% K+30% I+60%M.



M. e. of KOH/100 *g. of* H-*clay.*

FIG. 6. 10% K+10% I+80%M.

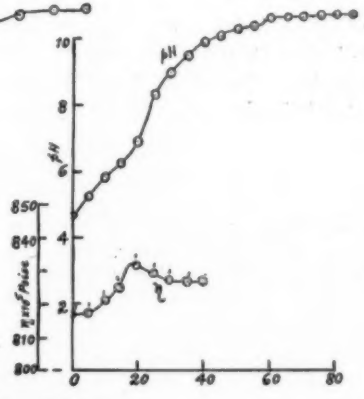


FIG. 7. 10% K+80% I+10%M.

Measurement of Cationic Activity

K^+ ion and Ca^{2+} ion activity—base saturation curves of ternary mixtures, symbolised as a_{k^+} and $a_{ca^{2+}}$ curves, are shown in Figs. 2-5 and the corresponding data in Table III.

TABLE III

Cationic fractions active in relation to clay minerals in mixtures.

Samples.		Assumed (m.e./100 g.).	Cation.	Fraction active. 25%.	50%.	75%.	Saturation. 100%.	125%.
Kaolinite	80%	18	K^+	0.40	0.220	0.200	0.190	0.180
Illite	10							
Montmorillonite	10	18	Ca^{2+}	0.09	0.044	0.032	0.033	0.030
Kaolinite	40	38	K^+	0.21	0.110	0.100	0.110	0.140
Illite	20							
Montmorillonite	40	45	Ca^{2+}	0.07	0.017	0.008	0.013	0.014
Kaolinite	40	27	K^+	0.22	0.110	0.100	0.110	0.150
Illite	40							
Montmorillonite	20	35	Ca^{2+}	0.06	0.020	0.011	0.017	0.018
Kaolinite	10	57	K^+	0.11	0.070	0.060	0.080	0.110
Illite	30							
Montmorillonite	60	65	Ca^{2+}	0.02	0.006	0.004	0.006	0.007

A comparison of a_{K^+} and $a_{Ca^{2+}}$ of the ternary mixtures indicates that the dissociation of these ions from these mixtures depends on the relative proportions of the individual clay mineral present. Thus, it has been observed that the mixture, which contains a larger amount of kaolinite, shows a higher cationic dissociation compared to the one which contains more of montmorillonite (Chatterjee and Marshall, *J. Phys. Coll. Chem.*, 1950, **54**, 671).

The works incorporated in this paper as also in Part I have been carried out under the scheme—"Studies on clay mineral contents of Indian soil", jointly financed by the Indian Council of Agricultural Research, Government of India and the Ministry of Agriculture, Government of West Bengal, to whom the authors acknowledge their grateful thanks.

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Received August 21, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1951]

Polarographic Study of Photoisomerisation of *o*-Nitrobenzaldehyde

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Kinetics of the photochemical reaction of *o*-nitrobenzaldehyde has been studied polarographically in the range of 4360 to 3130 Å. The aldehyde is reduced at the dropping Hg electrode and *C-V* curve with well-defined diffusion range is obtained.

Photoisomeric change of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid under the influence of light in the range 4360 to 3130 Å has been observed by Leighton and Lucy (*J. Chem. Phys.*, 1934, **6**, 498). The present investigation is undertaken to study the kinetics of this photochemical reaction polarographically. *o*-Nitrobenzaldehyde is found to be reduced at the dropping mercury electrode and current-voltage (*C-V*) curve with well-defined diffusion range is obtained. Diffusion current is found to be proportional to the concentration of *o*-nitrobenzaldehyde. Influence of sunlight on *C-V* curve of *o*-nitrobenzaldehyde is observed due to isomeric change of the same. The decrease of wave height of *C-V* curve of *o*-nitrobenzaldehyde under the influence of light has been interpreted and applied in the study of the reaction kinetics of photoisomeric change of the same.

EXPERIMENTAL

All measurements were made against saturated calomel electrode. The solution was deoxygenated by passing hydrogen through the solution. Same jet tube was used for dropping mercury electrode throughout the experiment.

Drop time of mercury was adjusted to 4-5 seconds per drop. All the chemicals used were analytical reagent (AnalaR). *o*-Nitrobenzaldehyde was purified by the method adopted by Leighton and Lucy (*loc. cit.*).

A known volume of a solution of 25% acetone in 0.01*N*-HCl—0.1*N*-KCl was electrolysed. An increasing potentials in the range of 0 to 1.33 volts (vs. S.C.E.) were applied to the cell and corresponding currents were noted. Current was plotted against the corresponding applied voltage (vs. S.C.E.) and *C-V* curve was obtained. To the same solution various amounts of 4.0×10^{-3} *M* *o*-nitrobenzaldehyde solution were added from a calibrated burette and polarograms were taken for different concentrations of *o*-nitrobenzaldehyde. Diffusion current at each concentration of *o*-nitrobenzaldehyde was determined from *C-V* curve, subtracting the current for blank. The electrolysis vessel was kept covered with a black paper during the measurements of current-voltage. It should be noted that the reduction potentials of acetone and aldehyde (Adkins and Cox, *J. Amer. Chem. Soc.*, 1938, **60**, 1151) group of *o*-nitrobenzaldehyde are beyond the range of potential applied. Moreover, no photochemical decomposition of acetone could be detected polarographically within the above range of applied voltage.

To study the reaction kinetics of photoisomerisation of *o*-nitrobenzaldehyde, the following procedure was adopted,

A polarogram of *o*-nitrobenzaldehyde (4.5×10^{-4} *M*) in 25% acetone, 0.01*N*-HCl, and 0.1 *N*-KCl was taken initially. It was then exposed to direct sunlight with constant stirring for definite intervals of time, namely, 10, 21, 30, 60, and 120 minutes and polarograms were taken after each exposure. Wave height was found to decrease successively at each exposure initially, but it remained unchanged in the later stages when the entire amount of *o*-nitrobenzaldehyde was converted into *o*-nitrosobenzoic acid. Diffusion current from each polarogram was measured from the wave height, subtracting the current from blank.

TABLE I

Relation of diffusion current to the conc. of o-nitrobenzaldehyde in 25% acetone, 0.01 N-HCl, and 0.1N-KCl.

At 0.6 volt (vs. S.C.E.). Galv. sensitivity = 4.3×10^{-8} amp./mm.

Conc. ($c\times104M$)	1.00	1.95	2.86	3.72	4.55
Diffusion current (deflection in cm).	2.3	4.7	6.7	8.7	10.7

DISCUSSION

As the concentration of the aldehyde was increased, the wave height also increased (Fig. 1). Table I shows that the concentration bears a linear relation with diffusion current

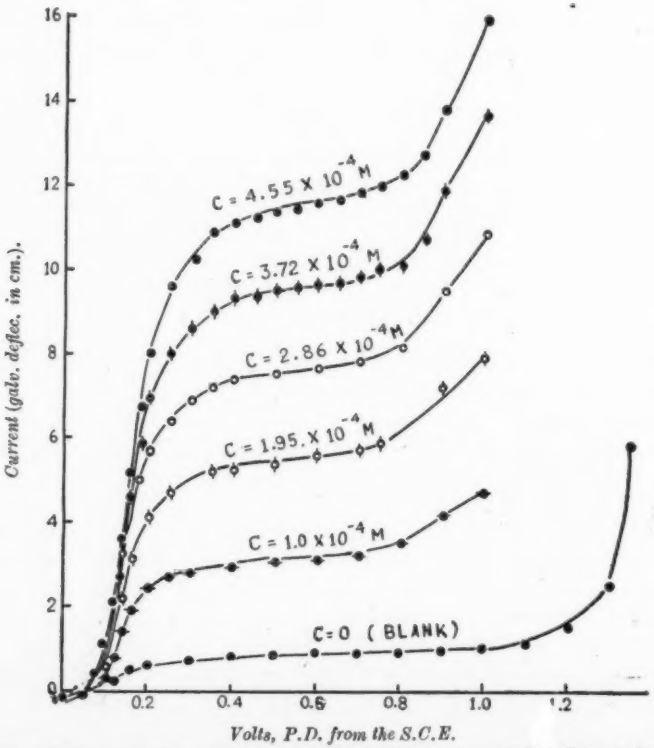


FIG. 1. Polarograms for *o*-nitrobenzaldehyde in 25% acetone+0.01*N*-HCl+0.1*N*-KCl. c=conc. of the aldehyde.

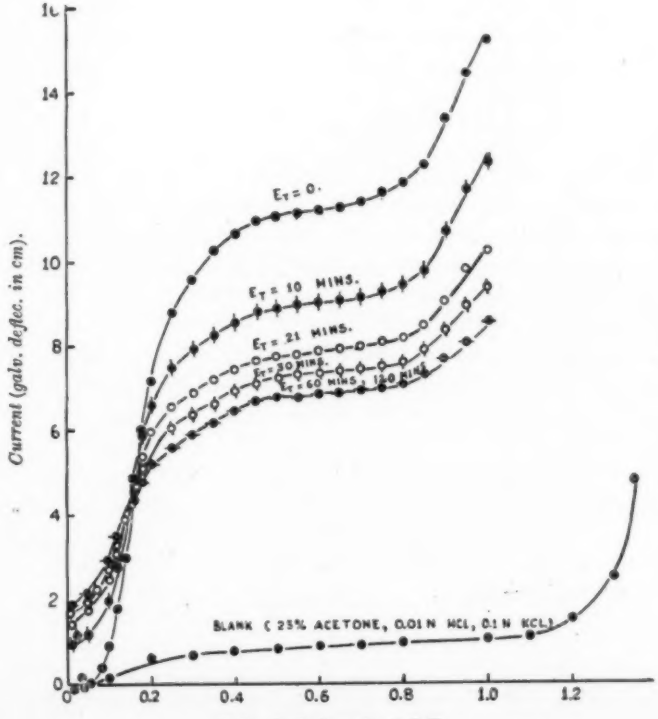
of *o*-nitrobenzaldehyde according to the Ilkovic equation (*Coll. Czech. Chem. Comm.*, 1934, **6**, 498). The decrease of wave height, *i.e.*, the diffusion current of *o*-nitrobenzaldehyde on exposure to light, is due to isomeric change of the same to *o*-nitrosobenzoic acid (cf. Fig. 2). Theoretically a linear relation should hold between the decrease of diffusion current and the amount of *o*-nitrobenzaldehyde isomerised by light. This enables us to study the kinetics of the photochemical reaction. The value of specific reaction rate (k) for first order reaction was calculated (cf. Table II).

TABLE II

Kinetics of photoisomerisation of o-*nitrobenzaldehyde in* 25% *acetone*, 0.01*N*-HCl *and* 0.1*N*-KCl.

Initial conc. of *o*-nitrobenzaldehyde $=4.5\times10^{-4}M$. Temp. $=30°$. $a = i_{d_0}-i_{d_\infty}=43$.

Time. (t)	Diffusion current (i_d). Galv. deflection.	$a-x=i_{d_t}-i_{d_\infty}$	Log $(a-x)$.	$k=\frac{2.303}{t}\log\frac{a}{a-x}$.
0 min.	103 mm			
10	81	21	1.3222	0.07168
21	70	10	1.0000	0.06900
30	65	5	0.7404	0.06860
60	60	..	..	..
∞	60	..	..	..



Volts, P.D. from the S.C.E.

FIG. 2. Influence of sunlight on *o*-nitrobenzaldehyde.
E_T=Time for exposure to light.

According to Leighton and Lucy (*loc. cit.*) this photochemical reaction of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid proceeds entirely by an intramolecular rearrangement with no side or reverse reaction. The course of electrolytic reduction of aromatic mononitro compounds was investigated by Haber (*Z. physikal. Chem.*, 1900, **32**, 271).

Employing nitrobenzene as an example, the main stages of the reduction in alkaline and acid solutions are: nitrobenzene → nitrosobenzene → phenylhydroxylamine → aniline. The final stage of reaction therefore would be

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O \quad .. \quad (1)$$

The reduction of nitrosobenzene to aniline is represented as:

$$C_6H_5NO + 4H = C_6H_5NH_2 + H_2O \quad .. \quad (2)$$

On the same line it may be assumed that electrolytic reduction of nitro group of *o*-nitrobenzaldehyde is as:

$$C_6H_4(NO_2).CHO + 6H = C_6H_4(NH_2).CHO + 2H_2O \quad .. \quad (3)$$

and that of photoisomerised *o*-nitrosobenzoic acid is

$$C_6H_4(NO).CO_2H + 4H = C_6H_4(NH_2).CO_2H + H_2O \quad .. \quad (4)$$

It is clear from equations (3) and (4) that nitro group of *o*-nitrobenzaldehyde in order to be reduced to amino group requires 6 hydrogen atoms, whereas nitroso group requires 4 hydrogen atoms. In the process of electro-reduction, the current detected is due to discharge of ions (here hydrogen ions). So diffusion current of *o*-nitrobenzaldehyde should decrease on irradiating the substance since concentration of *o*-nitrobenzaldehyde (in reduction $6H^+$ involved) decreases due to conversion to *o*-nitrosobenzoic acid (in reduction $4H^+$ involved). When the conversion is complete, there should be no further decrease of diffusion current as it will be then given solely by the reduction of *o*-nitrosobenzoic acid. It appears from Fig. 2 that the half-wave potentials of the both isomeric forms are very near to each other. The decrease of diffusion current should be proportional to the amount of *o*-nitrobenzaldehyde isomerised by light. The proposed mechanism has been justified by the determination of specific reaction rate, *k*, of photoisomerisation of *o*-nitrobenzaldehyde (cf. Table II). The value is fairly constant on the consideration of probable slight variation of intensity of sunlight during the whole operation.

The present investigation further reveals that polarographic method of analysis with a suitable electro-reducible substance may be employed to determine the total quantity of light that causes a photochemical reaction. Hence a polarograph may be used as an actinometer.

Author's thanks are due to Prof. S. S. Joshi, D.Sc., F.R.I.C., F.N.I., for suggesting the problem and to Dr. S. M. Deshpande for his valuable guidance and encouragement during the course of the work undertaken in the chemical laboratories, College of Science, Banaras Hindu University. His thanks are also due to Prof S. K. Mukherjee, D.Sc., for his kind help in preparing the note.

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Received June 26, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Studies on 2-Thiophenaldehyde: Condensation with Some Reactive Methylene Compounds

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2-Thiophenaldehyde has been condensed with malonic, malonanilic, and malon-*o*-, -*m*- and -*p*-toluidic acids using a trace of an organic base like pyridine or piperidine or an equimolar amount of glacial acetic acid as condensing agent; the products obtained have been identified.

The application of the "trace base method" of Pandya and coworkers (this *Journal*, 1934, **9**, 825; *Proc. Ind. Acad. Sci.*, 1935, **2A**, 402) to condensations of various aldehydes including furfuraldehyde and aliphatic aldehydes with malonic acid (George, Ph.D. thesis, Agra University, 1954) revealed a decrease in reactivity with decrease in "aromaticity" of the aldehyde. So it appeared interesting to investigate the behaviour of 2-thiophenaldehyde, which closely resembles aromatic aldehydes (Bidermann, *Ber.*, 1886, **19**, 639; Dunn and Dittmar, *J. Amer. Chem. Soc.*, 1946, **68**, 2561). This method gives much better yield than the other methods used by earlier workers (Bidermann, *Ber.*, 1886, **19**, 1855; Barger and Eason, *J. Chem. Soc.*, 1938, 2100., King and Nord, *J. Org. Chem.*, 1949, **14**, 405; 1950, **15**, 988).

In such condensations 2-thiophenaldehyde would appear to be slightly less reactive than benzaldehyde, since in the former the carbonyl group is linked to the high electron density centre (Fieser and Fieser, "Organic Chemistry", 2nd ed., 1950, p. 852) as contrast to the electron-accepting phenyl group in the latter. But the present investigation reveals that the reaction goes much faster than that with benzaldehyde (Pandya and Miss Pandya, *Proc. Ind. Acad. Sci.*, 1941, **14A**, 112) under the same experimental conditions. The effect of substituents on benzaldehyde in condensation with malonic acid, reported by Pandya and Vahidy (*ibid.*, 1936, **4A**, 140), also reveals that the same type of 'anomalous behaviour", viz., a methoxy substituent, which would make the phenyl group an electron donor, appears to have a favourable influence on the condensation. These observations are apparently contradictory to the current accepted mechanism of Perkin's reaction, viz., an electrophilic attack by the carbonyl carbon atom on the active methylene group.

When 2-thiophenaldehyde is condensed with malonic acid in presence of traces of pyridine or even piperidine, the non-decarboxylated product (2-thenalmalonic acid) is obtained.

Condensations of the above aldehyde with malonanilic and malon-toluidic acids give the decarboxylated products in presence of piperidine as the catalyst though not with pyridine.

2-Thenalmalonic acid and 2-thenalmalonanilic acid were decarboxylated by gently refluxing with a mixture of pyridine and piperidine to afford 2-thienylacrylic acid and 2-thienylacrylanilide respectively. $\alpha\beta$-Dibromo-2-thenalmalonic acid was prepared by direct addition of bromine to 2-thenalmalonic acid.

A study on the efficiency of pyridine, piperidine, 2,4-lutidine, and glacial acetic acid as condensing agents shows that they exert a catalytic effect, though one cannot say that one has greater effect than the other in all the reactions. Thus lutidine, a good condensing agent in condensations with malonic acid, is found to be not so efficient with malonanilic or malon-toluidic acids. Again glacial acetic acid, which is a poor condensing agent for the former, furnishes almost quantitative yields in the latter cases.

EXPERIMENTAL

2-Thenalmalonic Acid—.(*a*). A mixture of 2-thiophenaldehyde (1.1 g.), malonic acid (1.0 g.), and pyridine (0.1 c.c.) was heated in a small flask at 100° for 40 minutes. The mixture first melted to a light green liquid, but it soon solidified. After cooling this was extracted with a strong solution of sodium bicarbonate. The whole mass dissolved in the alkali solution. It was then washed with ether and the aqueous layer on acidification gave a white precipitate, which on purification by recrystallisation from ethanol yielded 1.4g. (74%) of 2-thenalmalonic acid, m.p. 206° (decomp.). It is sparingly soluble in water in the cold but dissolves readily in hot water and in ethanol. (Found: S, 15.85; equiv., 99. Calc. for $C_8H_6O_4S$:-S, 16.16%; equiv., 99).

(*b*). In a subsequent experiment the yield of 2-thenalmalonic acid rose to 98% when the reaction mixture, prepared as above, was kept at room temperature for an hour prior to heating at 100° for 40 minitues. Piperidine and lutidine in traces as well as an equimolar amount of glacial acetic acid were also used as condensing agents in place of pyridine. The results obtained are shown in Table I.

TABLE I

Catalyst.	Time of heating.	Temperature.	Yield %.
Nil	24 hrs.	Room temp.	3.4
,,	1	100°	52.0
Pyridine	24	Room temp.	48.0
,,	1	100°	80.0
,,	40 mins.	,,	98.0 (*b*)
Piperidine	30	,,	76.0
2,4-Lutidine .	30	,,	85.0
Gl. acetic acid	1 hr.	,,	58.0

2-Thienylacrylic Acid.—A mixture of 2-thenalmalonic acid (1 g.), pyridine (4. c.c.), and piperidine (4 drops) was gently refluxed for 30 minutes, cooled, and treated with

excess of HCl (conc.). The precipitated material was filtered, dissolved in sodium bicarbonate solution, and reprecipitated by acid. It was further purified by recrystallisation from ethanol when 0.66g. (85%) of 2-thienylacrylic acid, m.p. 144°, was obtained. (Found: S, 20.70; equiv., 154.4. Calc. for $C_7H_6O_2S$: S, 20.77%; equiv., 154.0).

∝β-Dibromo-2-thenalmalonic Acid.—Bromine (4 g.) in glacial acetic acid (5 c.c.) was added slowly with shaking to a solution of 2-thenalmalonic acid (1 g.) in hot glacial acetic acid (30 c.c.). The flask was then loosely corked and set aside for 5 days. A dark brown solid separating was filtered. A further crop of the same material was obtained on diluting the filtrate with water. These were then recrystallised from ethanol to yield 1.2 g. of ∝β-dibromo-2-thenalmalonic acid, m.p. 225°. (Found: S, 9.18. Calc. for $C_8H_6O_4Br_2S$: S, 8.94%).

2-Thenalmalonanilic acid (m.p. 212°) was obtained in 87% yield from malonanilic acid by the same procedure as with 2-thenalmalonic acid, the time of heating being 4 hours. 10% NaOH solution was used for extracting the reaction product as it was insoluble in sodium bicarbonate solution. (Found: S, 11,70; equiv., 273. 1. Calc. for $C_{14}H_{11}O_3NS$: S, 11.72%; equiv., 273).

2-Thienylacrylanilide.—Repetition of the above experiment, using a trace of piperidine in place of pyridine as the condensing agent, gave 2-thienylacrylanilide, m.p. 148°. (Found: S, 14.26. Calc. for $C_{13}H_{11}ONS$: S, 13.97%). It was also prepared by decarboxylating 2-thenalmalonanilic acid by refluxing the latter with an excess of pyridine containing a few drops of piperidine; yield 97.5%..

TABLE II

Yields of the products obtained in the condensation with malonanilic acid and malon-*o*-, *m*-and *p* toluidic acids.

Catalyst.	Malonanilic acid.		Malon-*o*-toluidic acid.		Malon-*m*-toluidic acid.		Malon-*p*-toluidic acid.	
	%Yield.		%Yield.		%Yield.		%Yield.	
	2-Thenal-X.	2-Thenyl-Y.	2-Thenal-X.	2-Thenyl-Y.	2-Thenal-X.	2-Thenyl-Y.	2-Thenal-X.	2-Thenyl-Y.
Nil	64	..	78	..	63	..	70	..
Pyridine	87	..	94	..	51	..	94	..
2,4-Lutidine	62	..	66	..	59	..	70	..
Piperidine	..	98	..	100	3	93	..	99
Gl. acetic acid	100	..	100	..	90	..	100	..

X stands for-malonanilic or -malontoluidic acid.
Y stands for acrylanilide or -acryltoluidide.

*Condensation with Malon-*o-,m- *and* p-*toluidic Acids.*—The procedure for these condensations was the same as that described for malonanilic acid. The following products were isolated:

2-Thenalmalon-*o*-toluidic acid, m.p. 216°. (Found: S, 11.48. equiv. 286, $C_{15}H_{13}O_3NS$ requires S, 11.2%, equiv. 287.)

2-Thienylacryl-*o*-toluidide, m.p. 142°. (Found: S, 12.9. $C_{14}H_{13}ONS$ requires S, 13.12%).

2-Thenalmalon-*m*-toluidic acid, m.p. 187°. (Found: S, 11.38. equiv. 286·5; $C_{15}H_{13}O_3NS$ requires S, 11.2%, equiv. 287).

2-Thienylacryl-*m*-toluidide, m.p. 138°. (Found: S, 12.8. $C_{14}H_{13}ONS$ requires S, 13.1%).

2-Thenalmalon-*p*-toluidic acid, m.p. 222°. (Found: S, 11.3, equiv. 286·8; $C_{15}H_{13}O_3NS$ requires S, 11.2%, equiv. 287).

2-Thienylacryl-*p*-toluidide, m.p. 138°. (Found: S, 12.98. $C_{14}H_{13}ONS$ requires S, 13.1%, equiv. 287).

Yields obtained with various condensing agents used are shown in Table II.

The authors are very grateful to the Scientific Research Committee, Uttar Pradesh, for a research grant.

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Received June 3, 1969.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Viscometric Study of Clay-humus Complexes

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Viscometric studies of clay-humus complexes have been made in the presence of different cations. The η_{sp}/C vs. C graphs are found to be linear, especially at high dilutions. An attempt has been made to obtain a rough idea about the molecular weights of the products of the reaction between clay and humus, using Staudinger's equation.

Clays are crystalline aggregates. Humic acid may perhaps be considered as mixtures of high polymers. Viscosity measurements have been undertaken with a view to obtain evidence of the interaction between clay and humic acid, if any. Myeres (*Soil Sci.*, 1937, **44**, 331) observed a considerable change in the time of flow of colloidal clay when it was mixed with organic colloidal sols; this change could not be explained by assuming simple mechanical mixing.

EXPERIMENTAL

An Ostwald viscometer in its simplest form was used. The time of flow of water at the temperature of experiment (30°) was 45 secs. Crude humic acid was extracted from Silguri soil from Darjeeling, West Bengal by repeated treatment with $(N/2)Na_2CO_3$ solution. From the alkali leachate humic acid was coagulated by HCl (dil.) and finally purified by electrodialysis. The clay fractions ($<1\,\mu$) from four different soil samples were collected in the usual way. The clay suspension was then coagulated with HCl (dil.), thoroughly treated with H_2O_2 to destroy organic matter, and finally electrodialysed to obtain H-clay. The humic acid and clay fractions were mixed in the proportions of 1:60 in presence of different ions and about a week's time was allowed for the reaction to proceed. The time of flow of the different mixtures was measured in the same Ostwald viscometer at a constant temperature of 30°. The viscosities of different clay-humic acid mixtures in presence of metal and H^+ ions were measured with various amounts of solid matter present in the suspension and the values of specific viscosities were calculated. Similar viscosity data for clays in presence of different ions, but without humus, were also obtained for comparison with the above results. The variation of reduced viscosities of all the systems with dilution was followed graphically by plotting η_{sp}/C vs. C.

DISCUSSION

The viscosity of dilute suspensions of rigid spherical particles, which are wetted by the solvent, is given by Einstein's equation

$$\eta/\eta_0 = 1+2.5\Phi+4\Phi^2+5{\cdot}3\Phi^3$$

from which $\eta_{sp} = (\eta/\eta_o - 1) = 2.5\Phi$, for small Φ (Φ=total volume of suspended particle/total volume of suspension). For non-spherical particles at higher concentrations, Guth *et al.* (*Kolloid Z.*, 1936, **74**, 266) obtained the following relation,

$$\eta = \eta_o (1 + 2.5\Phi + 14.1\Phi^2 + ..)$$

so that $\eta_{sp} = 2.5\Phi + 14.1\Phi^2$. If the unit of concentration is g./100 c.c. of suspension, $(\eta_{sp}/C)C \rightarrow O = (\eta)$, called the intrinsic viscosity, is equal to $0.025V$, where V is the specific volume of the solute. For swelling particles $(\eta) = 0.025SV$, where S is the swelling factor and is equal to effective volume, including bound and trapped solvent, divided by the actual volume. For prolates and oblates, the numerical factor 0.025 will increase according as the axial ratio becomes greater than unity. The values of (η) for the different systems have been obtained from the plot of η_{sp}/C vs. C, typical graphs of which are shown in Figures 1-4. The (η) values thus obtained are recorded in Table I.

TABLE I

CI=Illitic clay from Contai soil.
AGM=Montmorillonite clay from Aquagel.
KI=Illitic clay (with a trace of kaolinite) from Kakdwip soil.
RK=Rajmahal kaolinite.
SHm=Humic acid from Siliguri soil.

	CI.	AGM.	KI.	RK.
Humic acid	0.21	0.21	0.21	0.21
Clay	0.08	0.29	0.155	0.09
Clay + Ca^{2+}	0.09	0.33	0.20	0.11
Clay + Mg^{2+}	0.10	0.35	0.22	0.11
Clay + Al^{3+}	0.11	0.38	0.24	0.12
Clay + Fe^{3+}	0.12	0.40	0.24	0.13
SHm + clay + H^+ (1:60)	0.095	0.225	0.10	0.105
SHm + clay + Ca^{2+}	0.18	0.37	0.19	0.120
SHm + clay + Mg^{2+}	0.19	0.46	0.20	0.145
SHm + clay + Al^{3+}	0.22	0.72	0.22	0.160
SHm + clay + Fe^{3+}	0.23	0.80	0.23	0.170

If the density of humic acid is of the order of 1.2, S, the swelling factor=10.0, assuming spherical particles. For clays the density is of the order of 2.5 and S is of the order of 22, which indicates a much higher swelling than that of humic acid. For clay: humic acid ratio of 1:60, used in these experiments, the density of the mixtures may be taken to be equal to that of the clay itself. Consequently, any value of (η) greater than that of the clay would indicate extra swelling and/or inclusion of trapped water. In fact, except the AGM-SHm mixtures and KI-SHm mixtures containing H^+ ions, all the other systems indicate strong swelling and/or inclusion of trapped water. The values of S, calculated on the basis of $V = 1/2.5$, are recorded in Table II.

TABLE II

	CI.	AGM.	KI.	RK.
Clay	8.0	29.0	15.5	9.0
Clay + SHM + H^+	9.5(35)	22.5(55)	10.0(32)	10.5(23)
Clay + SHm + Ca^{2+}	18.0(46)	37.0(73)	19.0(42)	12.0(32)
Clay + SHm + Mg^{2+}	19.0(55)	46.0(82)	20.0(48)	14.5(37)
Clay + SHm + Al^{3+}	22.0(54)	72.0(82)	22.0(48)	16.0(36)
Clay + SHm + Fe^{3+}	23.0(58)	80.0(83)	23.0(50)	17.0(38)

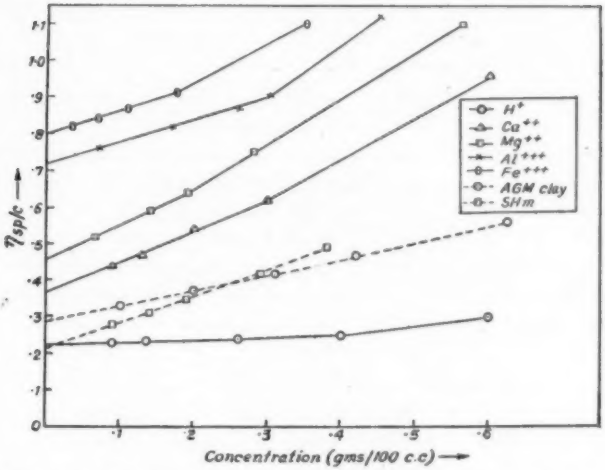

FIG. 1. AGM-clay—SHm mixtures in presence of diff. ions (SHm: AGM=1:60).

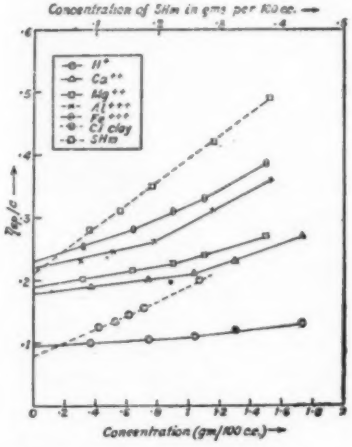

FIG. 2. CI-clay—SHm mixtures in presence of diff. ions (SHm: CI=1:60).

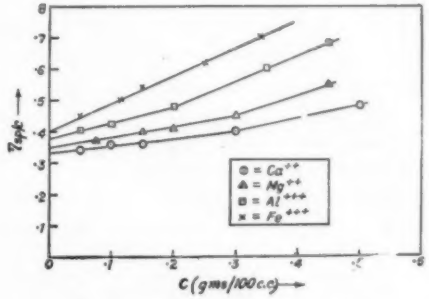

FIG. 3. AGM-clay+matal ions (without humic acid).

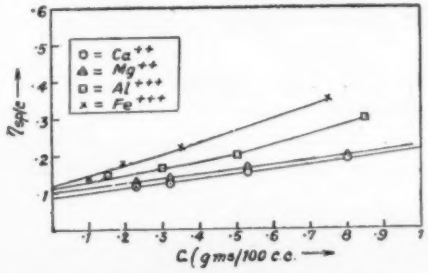

FIG. 4. CI-clay+metal ions (without humic acid).

The figures within brackets in Table II give the percentage of humic acid combined with clay at 1:60 ratio, which have been observed from the study of its adsorption on different clays (Sen, this *Journal*, 1960 **37**, 793).

It will be observed from the above figures that the swelling factor increases, with the exception of AGM and KI mentioned above, in the order: $H^+ < Ca^{2+} < Mg^{2+} < Al^{3+} < Fe^{3+}$. But the percentages of humic acid combined are in the order: $H^+ < Ca^{2+} < Mg^{2+} \approx Al^{3+} \approx Fe^{3+}$. It may be therefore that the increase in hydrodynamic volume or the swelling factor is not entirely due to the clay-humus complex, but may be also partly due to hydration of the ions themselves, which are likely to form flocculent masses with the clays or the clay-humus complexes. It will, however, be noted from the data in Table I that only with AGM and KI, the cations have an appreciable effect on (η), hence on the swelling or hydration of the clay. For the other clays, there is hardly any influence of cations on swelling.

If it is assumed that the flocculating effect of ions, *i.e.*, the secondary effect of ions causing increase in (η), is not exhibited to any marked extent in presence of Ca^{2+} ions, which mainly co-ordinate the clay and humic acid particles to form the complexes, the values of (η) may be used to get an idea of the molecular weight of such complexes. The molecular weight of humic acid (S. A. Waksman, "Humus") has been estimated at about 1500. This would correspond to a value of K in Staudinger's equation, $(\eta) = K.M^{\alpha}$, of the order of 5×10^{-3}, if α is assumed to be equal to 0.5. For clays and clay—humus complexes, if K is taken to be one tenth of that of humic acid, *i.e.*, $= 5 \times 10^{-4}$, M is of the order of 3×10^5 or more. Unless verified by independent methods, these values are of little use. Taking the values of $K = 5 \times 10^{-4}$ for AGM clay—humic acid mixtures, the molecular weight of the complex in presence of Fe^{3+} ions is of the order of 2.5×10^6, which is ten times larger than that of AGM clay itself. This may be taken to suggest that fairly large aggregates are formed between clay and humic acid.

With AGM clay—SHm mixtures, the molecular weight of the clay—humic acid complex in presence of H^+ ions appears to be less than that of the clay itself, although greater than that of crude humic acid. AGM clay is highly hydrated as the high value of hydrodynamic volume in Table II shows; a combination with humic acid in presence of H^+ ions probably reduces the number of entrapped solvent molecules and hence the value of (η). In presence of Ca^{2+} ions, the hydration considerably increases and therefore also the values of (η). So also is the case of KI clay.

The above calculation, owing to obvious limitations and lack of supporting data for the constants of Staudinger's equation, leads us to no definite and concrete understanding of the molecular species. There is, however, one point to be noted. The linear nature of the $\eta_{sp}C$ vs. C graphs, especially at high dilution, suggests strongly that the products of the interaction are quite stable and do not disaggregate on dilution, thus behaving more or less as molecular species.

Thanks are due to Prof. S. K. Mukherjee, D.Sc., Professor of Macromolecules, Indian Association for Cultivation of Science, for his guidance and valuable suggestions and to Prof. P. C. Rakshit, Ph.D., Head of the Department of Chemistry, Presidency College, Calcutta, for his continued interest and giving laboratory facilities.

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Received September 23, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Spectrophotometric Study of Ferric—mandelate Complex and its Photoreduction

S. D. Bhardwaj and G. V. Bakore

Mandelic acid (sodium salt) has been found to form a yellow-coloured complex with Fe^{3+}. The complex has the composition $(Mandelate^{-})_2\ Fe^{+}$ and has maximum absorption at 360 mμ between *p*H 1.0 and 6.0. The values of dissociation constant and ΔF are respectively 1.94×10 and -436.98 Kcal./mole at 25°.

During photo-reaction of iodine and α-hydroxy-acids in presence of metal ions like Fe^{3+} (Ph.D. thesis, Raj Univ., 1959), it was observed that the complexes of metal ion and α-hydroxy-acids played an important role.

In the present communication the spectrophotometric study of the system mandelate—Fe^{3+}, using various concentrations of the reactants has been made. The composition and the structure of the complex formed have been discussed; the dissociation constant and the free energy of formation of complex have been calculated at 25°.

EXPERIMENTAL

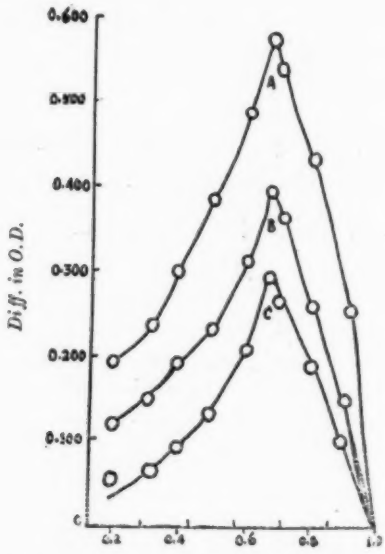
"AnalaR" ferric ammonium sulphate and mandelic acid were used. Other chemicals were also chemically pure. Solutions were made in double-distilled water. *p*H measurements were made with a Beckman *p*H meter (Model-H_2). Spectrophotometric measurements were made with a Beekman spectrophotometer (DU Model) with 1 cm cell at 25°±1°.

Validity of Beer's Law.—From a set of experiments, using different concentrations of Fe^{3+}, it was concluded that the Beer's law was rigidly obeyed between the concentration range of $M \times 10^{-1}$ and $M \times 10^{-3}$.

Nature of the Complex.—In another set of experiments, mixtures containing varying proportions of mandelate and ferric ammonium sulphate (1:1, 1:2, 1:3, 1:4, etc.) were prepared and the optical densities of the solutions at different wave lengths in each case were measured. In all the cases, the maximum absorption occurred at a spectral region of 360 mμ, thus indicating the formation of only one complex with the reagent (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63,** 437).

Stoichiometry of the Complex.—The composition was determined by Job's method of continued variations (*Compt. rend.*, 1928, **120,** 928). Measurements using equimolecular and non-molecular solutions in large number (total volume 50 c.c.) were made at 360 mμ. Some of the typical observations are plotted in Fig. 1, where the difference of optical densities of the mixture and Fe^{3+} in absence of the chelating agent is plotted against composition of the mixture. This is necessary because under these conditions ferric iron can also exist as ion pair $Fe(OH)^{2+}$ which has maximum absorption in the range of 300-450 mμ.

The peaks of the curves occur at a ratio of 2:1.



$[Mandelate]/\{[Fe^{3+}]+[Mandelate]\}$.

FIG. 1. A=[Mand]=$10\times10^{-3}M$; [Fe^{3+}]=$5\times10^{-3}M$.
B= „ =[Fe^{3+}]=$5\times10^{-3}M$.
C= „ = „ =$3.34\times10^{-3}M$.

Effect of p**H.**—Solutions containing the same concentrations of iron and mandelate were prepared at different *p*H. The *p*H of the mixture was varied in the range of 1.0 to 6.0. It was found that at all *p*H's used, the maximum absorption occurred at 360 mμ, thus indicating that the nature of the complex did not change in the *p*H range studied.

Sensitivity of the Complex.—Ferric—mandelate complex is stable in diffused room light. In the light from 1000 watt lamp, the complex, however, undergoes photodecomposition. Photodecomposition of the complex takes place in the sunlight as well.

DISCUSSION

Dissociation Constant of the Complex.—For determination of the dissociation constant, we have used the method employed by Mukherji and Dey (this *Journal*, 1957, **34**, 461). The difference in optical densities in presence and absence of mandelate is plotted against (Mandelate^{-1}) $\{[Fe^{3+}]+[Mandelate^{-1}]\}$. These plots are shown in Fig. 1. It may be assumed that in descending portion of the curve, when mandelate is in excess, most of the iron is bound in the complex and hence the observed optical density is mainly due to the colour of the complex. We may therefore assume that at points in the curves, where the optical densities are same, the amounts of the complex formed are indentical.

In the present case we have:

$$\underset{(a-2x)}{2MA^-} + \underset{(b-x)}{Fe^{3+}} \rightleftharpoons \underset{x}{\text{Complex}}$$

$$K = \frac{x}{(a-2x)\ (b-x)}.$$

Taking the two concentrations a_1 and a_2 and b_1 and b_2 for the rectants, giving the same optical density, we have

$$x = \frac{a_1b_1 - a_2b_2}{(2b_1a_1) - (2b_2a_2)}.$$

Knowing the values of x in the above equation, the value of $1/K$, which is the dissociation constant, can be calculated.

We have calculated the values of dissociation constant at optical density 0.300 in the curves A, B and C of Fig. 1 and the average value comes out to be 1.94×10^{-4} (un corrected for ionic strength) at 25°.

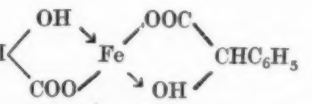
The free energy of formation can be obtained from the relation:

$$\triangle F = -RT\ln k$$

where the terms have their usual significance. In this system the value of $\triangle F$ at 25° works out to be-36.98 Kcal./mole.

Structure of the Complex.—The ratio of mandelate to iron in the mixture is 2 : 1. The wave lengths at which maximum absorption due to complex takes place does not change with *p*H in the range of 1.0 to 6.0. Further, the optical density at wave length of maximum absorption remains unaffected by changes in *p*H in the above range. These facts suggest that the iron-mandelate system can be represented as:

$$2.C_6H_5.CH(OH).COO^- + Fe^{3+} \rightleftharpoons$$



(It may be assumed that the remaining two co-ordination positions are occupied by water molecules).

Photoreduction of the Complex.—The following procedure was used to follow the photoreduction of iron—mandelate complex.

The 1000-watt lamp was run at constant voltage through a variac. Heat radiations were removed by using 0.2*M*-$CuCl_2$ solution. The reaction vessel was made of hard glass with parallel faces. The rate of photo-decomposition was studied spectrophotometrically by measuring the optical density at different time intervals. Since Beer's law is valid, the rate at which optical density changes is the measure of the photoreduction. Fig. 2 illustrates the results.

The rate at which the complex undergoes photoreduction follows zero-order law for early stages of the reaction, although towards the end the photoredution follows first order law.

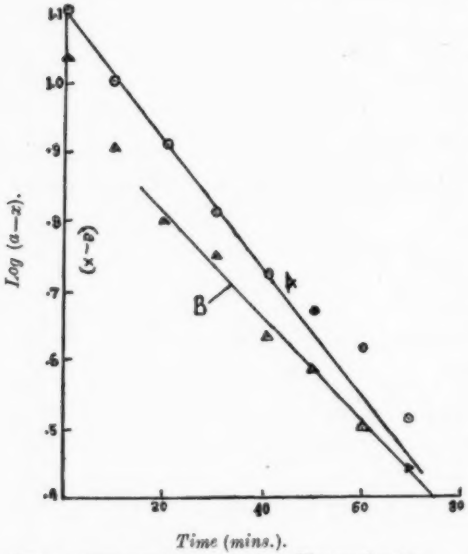


FIG. 2. Iron-mandelate complex: Photoreduction.
A=Zero order } [complex] = $30\times10^{-2}M$.
B=First order }

The photoreduction of the complex can be understood on the basis of the following reaction scheme:

$$Fe[H\text{-}Mandelate]_2^{+} \xrightarrow{K_e I_o} Fe^{2+}+R^{-}+CO_2$$

$$FeOH^{2+} \overset{K_e' I_o}{\rightleftharpoons} Fe^{2+}+OH$$

$$FeOH^{2+} \underset{K_s}{\overset{K_d}{\longrightarrow}} Fe^{2+}+OH$$

$$R^{-}+Fe\,[H\text{-}Mandelate^{-}{}_2]^{+} \longrightarrow Fe^{2+}+P$$

$$Fe^{3+}+OH^{-} \longrightarrow Fe^{2+}+OH^{-}$$

[where R is the radical and P is the product of oxidation of mandelic acid. K_e is the fraction of light absorbed by Fe [Mandelate$^{-}{}_2$] and I_o is the intensity of light; K_e'=fraction of light absorbed by $FeOH^{2+}$; K_s and K_d stand for the separation of the primary products and dark reaction].

That radical is produced by photo-irradiation of iron—mandelate complex is supported by the work of Levesley and Waters (*J. Chem. Soc.*, 1955, 217) on manganese pyrophosphate oxidation of ∝-hydroxy-acids. On this basis, the rate of photoreduction becomes

$$\frac{-d[Fe^{3+}]}{dt} = \frac{d[Fe^{2+}]}{dt} = 2K_e I_o + \frac{2K_s K_e' I_o}{(K_d+K_s)}$$

$$= 2\left(K_e + \frac{K_s K_e'}{K_d+K_s}\right) I_o$$

The rate expression shows that the rate is independent of concentration of the complex (*i.e.*, zero order). Since $K_e=(1-e^{-klc})>1$ when concentration is large (c=concentration of the complex; l=path length = 1 cm). When concentration becomes sufficently less, $K_e > Klc$ and the rate then becomes first order with respect to the complex.

Authors are grateful to Professor S. R. Palit, D.Sc., F.R.I.C., F.N.I., of the Indian Association for Cultivation of Science, for helpful discussion.

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Received August 14, 1961.

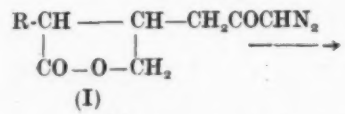
[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

A New Route to Pilosinine and *dl*-6-Ethylpilosinine

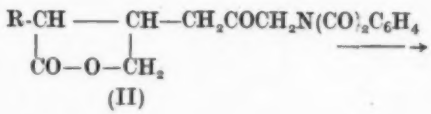
J. K. Mehrotra and A. N. Dey

A new method for aminomethylhomo-*r*-lactones as the starting materials for the preparation of pilosinine and *dl*-6-ethylpilosinine has been described. This has been achieved by hydrolysing the corresponding ethyl 1-substituted-3-phthalimidoacetoacetates.

Pilocarpine (IV: R=Et), the chief alkaloid of Jaborandi, has been found to consist of *r*-lactone and an imidazole joined through a methylene bridge. For the synthesis of pilocarpine and isopilocarpine, Preobrashenski *et al.* (*Ber.*, 1930, **63**, 460; 1933, **66**, 1536) obtained diazomethyl homopilopyl ketone (I: R=Et) from the chloride of pilopic acid. The former was transformed into the chloro derivative, which with potassium phthalimide gave phthalimidomethyl homopilopyl ketone (II: R=Et). On hydrolysis, the latter gave aminomethyl homopilopyl ketone (III: R=Et) which with KCNS yielded 2-thiol-pilocarpidine. This on oxidation with $FeCl_3$ and subsequent methylation gave pilocarpine (IV: R=Et). Following a similar procedure, Preobrashenski and Kuleshowa (*J. Gen. Chem., U.S.S.R.*, 1945, **15**, 237) have prepared a series of pilocarpine analogues.



(I)



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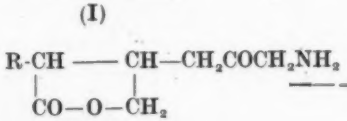

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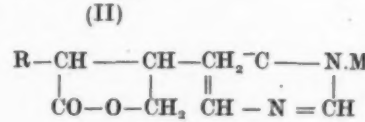
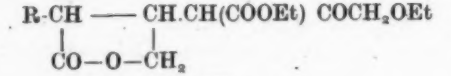


(IV)

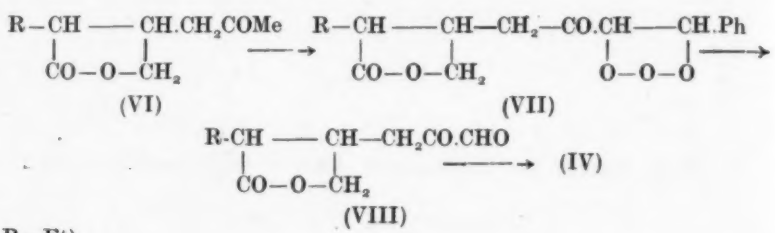
Dryamova *et al.* (*ibid.*, 1948, **18**, 1733) condensed 3-hydroxyisocrotonic acid lactone with ethyl *r*-ethoxyacetoacetate in presence of sodium ethoxide and obtained ethyl α-ethoxyacetylhomopilosinate (V: R=H). The latter was first hydrolysed by HCl (1:3) and then by HBr to furnish bromomethyl homopilosinyl ketone which with potassium phthalimide gave phthalimidomethyl homopilosinyl ketone [II: R=Et).



(V)

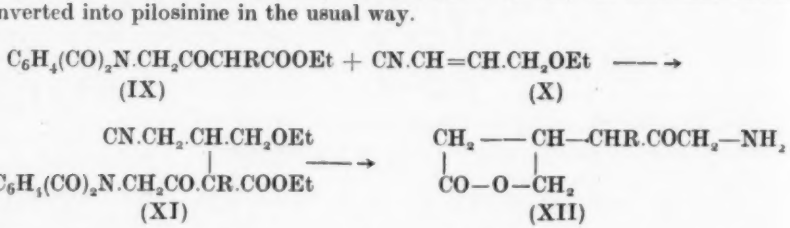
In an independent method Dey (*J. Chem. Soc.*, 1937, 1057), using methylzinc iodide, converted homopilopyl chloride into β-acetonyl- α-ethyl-*r*-butyrolactone (VI). The ozonide (VII) of the benzylidene derivative of the latter on decomposition gave a glyoxal (VIII),

which on treatment with ammonia and formaldehyde and subsequent methylation gave pilocarpine and isopilocarpine (IV : R=Et).

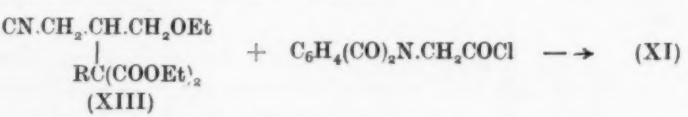


(where R=Et).

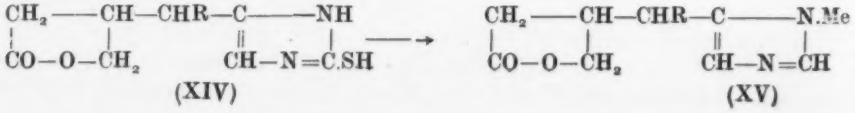
In the present investigation for the preparation of pilosinine (IV: R=H), a modified method for the preparation of aminomethyl homopilosinyl ketone (XII: R=H) has been followed. Ethyl 3-phthalimidoacetoacetate (IX : R=H) (Mehrotra and Verma, this *Journal*, 1961, **38**, 785) was condensed with 1-ethoxy-3-cyano-2-propene (X) in presence of NaOEt when a deep red product was produced, from which ethyl 1-phthalimidoaceto-2-ethoxymethyl-3-cyanobutyrate (XI : R=H) could not be crystallised. On hydrolysis of this product aminomethyl pilosinyl ketone [XII : R=H) was obtained. The latter was converted into pilosinine in the usual way.



In an attempt to obtain pure product (XI: R=H), an alternative procedure was followed. The propene (X) was condensed with diethyl malonate to afford ethyl 1-ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate (XIII : R=H). The ethoxymagnesium salt of this compound was condensed with phthalimidoacetyl chloride. The product on steam distillation furnished (XI: R=H) in good yield.



In another preparation, ethyl group was introduced in the methylene bridge of pilosinine. For this purpose, ethyl 1-ethyl-3-phthalimidoacetoacetate (IX : R=Et) (Dixit *et al.*, this *Journal*, 1961, **38**, 853) was condensed with (X) in presence of NaOEt to afford (XI: R=Et). After hydrolysis of the latter and treatment with KCNS, it gave *dl*-2-thiol-6-ethylpilosinidine (XIV : R=Et). This was oxidised and methylated to yield *dl*-6-ethylpilosinine (XV : R=Et).



EXPERIMENTAL

Aminomethyl Homopilosinyl Ketone.—In a three-necked flask were placed ethyl 3-phthalimidoacetoacetate (6.87g., 0.025*M*) and dry ethanol (50 c.c.) and the whole was warmed to dissolve the ester. To this a solution of sodium ethoxide (from 0.58 g. of Na) in 15 c.c. of ethanol was added dropwise with stirring. The deep red mixture was stirred for ½ hour more; 1-ethoxy-3-cyano-2-propene (2.78 g., 0.025*M*) in dry ethanol (15c.c.) was added during 30 minutes. After allowing the mixture to stand overnight, it was refluxed for 1 hour and cooled. Glacial acetic acid (1.52 g.) was added and the mixture stirred for 15 minutes. The solvent was removed at 40-50° and to the deep red syrupy residue water (20 c.c.) was added. This was extracted with 80, 10, and 10 c.c. portions of benzene. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed to yield 8.78 g. of a deep red residue. This was refluxed with 50% HCl (45 c.c.) for 10 hours in an oil bath at 140°. The mixture was cooled and filtered. The filtrate was evaporated under diminished pressure. The residue was dissolved in water and treated with decolorising charcoal. Water was again removed and the residue kept over solid NaOH in vacuum for 24 hours and then extracted with dry ether-ethanol (1:3; 10 c.c. ×3). From the organic liquid, the solvent was removed and the residue refluxed with 48% HBr (20 c.c.) for 10 hours in an oil bath at 145°. HBr was completely removed under diminished pressure. The residue was dissolved in dry ethanol (4 c.c.) and freezed when extremely hygroscopic crystals of *aminomethyl homopilosinyl ketone hydrobromide*, m.p. 138° (decomp.), was obtained in 3 g. yield- It was quickly filtered and dried in vacuum over P_2O_5. (Found: C, 35.39; H, 4.84; N, 5.88. Calc. for $C_7H_{12}O_3NBr$: C, 35.30; H, 5.04; N, 6.00%).

Ethyl 1-*Ethoxycarbonyl*-2-*ethoxymethyl*-3-*cyanobutyrate*.—In a 500 c.c. three-necked flask were placed dry ethanol (100 c.c.) and clean sodium (9.2 g.) and diethyl malonate (80 g.) was added to it, followed by dropwise addition of 1-ethoxy-3-cyano-2-propene (45.5 g.) during 45 minutes. The mixture was refluxed with continued stirring for 1½ hours and then cooled. Glacial acetic acid (25 g., 0.42*M*) was then added and the ethanol was removed. To the residue water was added (200 c.c.) and the lower layer of crude ester separated and dried over fused $CaCl_2$. This was fractionated, collecting 105 g. of the ethyl 1-ethoxycarbonyl-ester passing at 192-99°/20 mm, $d_{18.5}^{18.5}$ 1.0637; $n_D^{20.9}$ 1.439. (Found: C, 58.1; H, 8.5. $C_{13}H_{21}O_5N$ requires C, 57.56; H, 7.75%).

Ethyl 1-*Phthalimidoaceto*-2-*ethoxymethyl*-3-*cyanobutyrate*.— Clean magnesium turnings (4.8 g.), dry ethanol (7c.c.), and dry CCl_4 (1 c.c.) were taken in a three-necked flask and to it were added ethyl 1-ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate (54.2g.) and dry ethanol (20 c.c.) at such a rate that a vigorous reaction was maintained. When the reaction had subsided, dry ether (75 c.c.) was added and the mixture refluxed till all the magnesium had dissolved. The solvent was removed and the residue again dissolved in benzene (75 c.c.). The solvent was again removed and the residue was suspended in dry ether (75 c.c.) and phthalimidoacetyl chloride (44.8 g.) in dry ether (500 c.c.) was added with stirring at such a rate that a vigorous reaction was maintained. Finally the reaction mixture was gently refluxed for 2 hours, cooled in an ice bath, washed with water, and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was steam-distilled till a clear distillate was obtained. The residue was extracted with 100, 50 and 50 c.c. portions of benzene. The mixed organic layer was filtered and dried over fused $CaCl_2$. The solvent was completely removed and the residue tirturated with dry ethanol (10 c.c) and left overnight in an ice bath.

Crystals of the desired product (42 g.) were filtered and recrystallised from ethanol when it melted at 106-107°. (Found: C, 61.9; H, 4.8; N, 7.3. $C_{20}H_{22}O_6N$ requires C, 61.9; H, 5.2; N, 7.25%).

This ester (4 g.) when hydrolysed, as described above, gave 1.4 g. of *aminomethyl homopilosinyl ketone hydrobromide*, m.p. 138°. (Found: C, 35.39; H, 4.84; N, 6.08. Calc. for $C_7H_{12}O_3NBr$: C, 35.3; H, 5.04; N, 5.88%). This ketone on treatment with KCNS (2g.) in aqueous solution (0.83g.) gave 0.7 g. of *2-thiol-pilosinidine*, m.p. 202° (lit. m.p. 202.5°). The thiol (0.4 g.) was oxidised by heating with an aqueous solution $FeCl_3$ (2.8 g.) to yield 0.39 g. of white crystalline *pilosinidine nitrate*, m.p. 116° (lit. m.p. 117-18°). This salt (0.3g.) on methylation gave *pilosinine nitrate*, m.p. 168° (lit. m.p. 165-67°), yield 0.19 g.

dl-2-*Thiol*-6-*ethylpilosinidine*.—By following a procedure similar to that described above, ethyl 1-ethyl-3-phthalimidoacetoacetate (15.15 g.) was condensed with 1-ethoxy-3-cyano-2-propene (5.55 g.) using metallic sodium (1.15g.) and finally glacial acetic acid (3.3g., $>0.05M$). The condensed product was hydrolysed first by HCl (75 c.c.) and after the removal of phthalic acid and NH_4Cl, this was further hydrolysed by 48% HBr (40 c.c.). Aminoketone thus obtained was treated with an aqueous solution of KCNS (1.8g.) to yield 1.1 g. of the crystalline product, m.p. 221° (decomp.). (Found: C, 53.51; H, 6.07; N, 12.39; S, 14.6. $C_{10}H_{14}O_2N_2S$ requires C, 53.9; H, 6.19; N, 12.02; S, 14.16%).

dl-6-*Ethylpilosinine*.—The preceding compound (0.46g.) was oxidised by an aqueous solution of $FeCl_3$ (3 g.) and from the oxidised solution dl-6-*ethylpilosinidine nitrate*, m.p. 146° (with slight decomposition), was obtained; yield 0.36g. (Found: C, 46.51; H, 6.81; N, 16.12. $C_{10}H_{15}O_5N_3$ requires C, 46.51; H, 6.2; N, 16.28%). This nitrate (0.3g.) was made alkaline with 50% K_2CO_3 and extracted with $CHCl_3$ (15c.c. $\times 3$). The organic layer was dried and the solvent removed. The residue was methylated with methanol (2 c.c.) and CH_3I (0.5 c.c.) in a sealed tube at 50-60°. From this 0.28 g. of white crystalline dl-6-*ethylpilosinine nitrate*, m.p. 141-43°, was obtained. (Found: C, 48.25; H, 6.1; N, 15.70. $C_{11}H_{16}O_5N_3$ requires C, 48.53; H, 6.61; N, 15.44%).

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Received June 14, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961].

Chloromethylation of Some 5- and 6-Hydroxycoumarin Derivatives

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5-Hydroxy- and 6-hydroxy-4-methylcoumarins and their methyl ethers and methyl 5-hydroxy-4-methylcoumarin-6-carboxylate have been chloromethylated using different molecular proportions of paraformaldehyde. Structures of the chloromethylated coumarins have been established by comparison of the methyl derivatives, obtained on reduction, with compounds of known structures.

The work on the chloromethylation of coumarins, described earlier (*J. Org. Chem.*, 1960, **25**, 1713), has been extended.

Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate on chloromethylation with one mole of paraformaldehyde furnished a monochloromethyl derivative, which on reduction gave methyl 5-hydroxy-4,8-dimethylcoumarin-6-carboxylate, as seen on direct comparison with the compound synthesised as follows: 4-Methylresorcinol on carboxylation gave a monocarboxylic acid. This could either be 2,4-dihydroxy-5-methylbenzoic acid (A) or 2,6-dihydroxy-3-methylbenzoic acid (B). The methyl ester of (B) on the Pechmann condensation with ethyl acetoacetate would give a 7-hydroxycoumarin derivative. But the product actually obtained on the Pechmann condensation did not show any fluorescence, but gave a deep yellow solution with alkali, indicating that it was a 5-hydroxycoumarin derivative. The acid was therefore (A). Moreover, the Pechmann condensation product gave a deep reddish brown colour with ethanolic ferric chloride and so it was methyl 5-hydroxy-4,8-dimethylcoumarin-6-carboxylate and not the isomeric product, methyl 5-hydroxy-4,6-dimethylcoumarin-8-carboxylate. The monochloromethyl derivative is therefore methyl 5-hydroxy-8-chloromethyl-4-methylcoumarin-6-carboxylate.

Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate on chloromethylation with an excess of paraformaldehyde furnished a dichloromethyl derivative, which must be methyl 5-hydroxy-3,8-dichloromethyl-4-methylcoumarin-6-carboxylate, as there was no other possibility. This on reduction gave the corresponding trimethyl derivative, which on hydrolysis, decarboxylation and methylation yielded 5-methoxy-3,4,8-trimethylcoumarin.

5-Hydroxy-4-methylcoumarin on chloromethylation furnished a polymeric product. Its methyl ether on similar chloromethylation with one mole of paraformaldehyde gave a pure but chlorine-free product. The analysis indicated its identity as a methylene-bis-(5-methoxy-4-methylcoumarin). It has not been investigated further.

5-Methoxy-4-methylcoumarin on chloromethylation with an excess of paraformaldehyde furnished a dichloromethyl derivative. It was the 3,8-dichloromethyl derivative as on reduction it gave a product identical with 5-methoxy-3,4,8-trimethylcoumarin, mentioned earlier.

6-Hydroxy-4-methylcoumarin on chloromethylation with 1 to 2 moles of paraformaldehyde furnishes a monochloromethyl derivative to which the 5-chloromethyl structure has been tentatively assigned as the product obtained from it on reduction is different from 6-hydroxy-3,4-dimethylcoumarin (Robertson *et al.*, *J. Chem. Soc.*, 1931, 2426) and 6-hydroxy-4,7-dimethylcoumarin. The latter was prepared by the Elbs persulphate oxidation of 4,7-dimethylcoumarin. Attempts to synthesise 6-hydroxy-4,5-dimethylcoumarin by the Clemmensen reduction of 6-hydroxy-5-formyl-4-methylcoumarin, prepared according to Naik and Thakor (*J. Org. Chem.*, 1957, **22,** 1626), gave an unworkable product. The Sommelet reaction on the chloromethyl derivative gave a complex product. With an excess of paraformaldehyde 6-hydroxy-4-methylcoumarin gave a polymeric product.

6-Methoxy-4-methylcoumarin on chloromethylation with 1 to 3 moles of paraformaldehyde did not give a pure product. On chloromethylation with excess of paraformaldehyde it gave the 3,7-dichloromethyl derivative, which on reduction gave 6-methoxy-3,4,7-trimethylcoumarin, identical with the product obtained on methylation of 6-hydroxy-3,4,7-trimethylcoumarin, prepared by the Elbs persulphate oxidation of 3,4,7-trimethylcoumarin.

EXPERIMENTAL*

Methyl 5-Hydroxy-8-chloromethyl-4-methylcoumarin-6-carboxylate.—A mixture of methyl 5-hydroxy-4-methylcoumarin-6-carboxylate (4.68 g., 0.02*M*) in glacial acetic acid (40 c.c.), paraformaldehyde (0.72 g., 0.024*M*), and anhydrous zinc chloride (4.1 g., 0.03*M*) was heated on a steam bath and hydrogen chloride passed for 2 hours. The product separating was washed with ethanol and crystallised from benzene in colorless needles (0.5 g.), m.p. 215-17°. (Found: C, 55.2; H, 3.8; Cl, 12.7. $C_{13}H_{11}O_5Cl$ requires C, 55.2; H, 3.9; Cl, 12.6%).

Methyl 5-Hydroxy-4,8-dimethylcoumarin-6-carboxylate.—The above chloromethylcoumarin (0.5 g.) in acetic acid (80%, 20 c.c.) was heated with zinc dust (1 g.) at 60-70° for 2 hours. The product separating on dilution with cold water was refluxed with benzene (10 c.c.). The insoluble portion crystallised from acetic acid in needles, m.p. 229°. (Found: C, 62.7; H, 4.7. $C_{13}H_{12}O_5$ requires C, 62.9; H, 4.9%).

The same product was obtained when a mixture of methyl 2,4-dihydroxy-5-methylbenzoate (*vide infra*) (1.82 g.) and ethyl acetoacetate (1.30 g.) was treated with 80% H_2SO_4 (10 c.c.) and left overnight at room temperature. The product separating on pouring the reaction mixture in cold water was treated with sodium bicarbonate solution and the residue crystallised from rectified spirit.

2,4-Dihydroxy-5-methylbenzoic Acid.—A mixture of 4-methylresorcinol (10 g.), potassium bicarbonate (50 g.) and water (100 c.c.) was heated on a steam bath for 5 hours and then heated vigorously on a wire gauze for half an hour. The product separating on acidification was purified through sodium bicarbonate solution. It crystallised from hot water in shining yellow needles (4.5 g.), m.p. 212° (efferv.). (Found: C, 57.2; H, 4.8. $C_8H_8O_4$ requires C, 57.1; H, 4.8%).

* All melting points are uncorrected.

The *methyl ester*, prepared by refluxing the acid (10 g.) in methanol (50 c.c.) with H_2SO_4 (conc., 5 c.c.) for 10 hours, crystallised from benzene-petroleum ether mixture in needles (8.0 g.), m.p. 122-24°. (Found: C, 59.1; H, 5.5. $C_9H_{10}O_4$ requires C, 59.3; H, 5.5%).

Methyl 5-Hydroxy-3,8-dichloromethyl-4-methylcoumarin-6-carboxylate.—A mixture of methyl 5-hydroxy-4-methylcoumarin-6-carboxylate (2.34 g., 0.01 *M*) in glacial acetic acid (60 c.c.), paraformaldehyde (4.8 g., 0.16*M*), and anhydrous zinc chloride (4.1 g.; 0.03*M*) was treated with hydrogen chloride at 100° for 1 hour. The product separating was washed with ethanol and crystallised from benzene in needles (2.2 g.), m.p. 168°. (Found: C, 50.7; H, 3.6; Cl, 21.1. $C_{14}H_{12}O_5Cl_2$ requires C,50.8; H, 3.6; Cl, 21.5%).

The *diacetoxymethyl* derivative was prepared by refluxing the above chloromethylcoumarin in glacial acetic acid with fused sodium acetate for 2 hours. It crystallised from rectified spirit in needles, m.p. 125-27°. (Found: C, 57.2; H, 4.9. $C_{18}H_{18}O_9$ requires C, 57.1; H, 4.8%).

Methyl 5-Hydroxy-3, 4, 8-trimethylcoumarin-6-carboxylate.—The above dichloromethyl derivative (1 g.) in acetic acid (80%, 40 c.c.) and zinc dust (2 g.) were heated at 60-70° for 2 hours. The product obtained on dilution with cold water was refluxed with benzene (5 c.c.) for 5 minutes and filtered. The residue was crystallised from acetic acid in shining needles, m.p. 218°. (Found: C, 64.2; H, 5.3. $C_{14}H_{14}O_5$ requires C, 64.1; H, 5.3%).

5-Hydroxy-3,4,8-trimethylcoumarin-6-carboxylic Acid.—The above ester (0.5 g.) was heated on a steam bath for 1 hour with 10%NaOH solution (10 c.c.). The product obtained on acidification was purified through sodium bicarbonate treatment and crystallised from dilute acetic acid, m.p. 274° (efferv.). (Found: C, 62.8; H 4.7. $C_{13}H_{12}O_5$ requires C, 62.9; H 4.8%).

5-Hydroxy-3-4,8-trimethylcoumarin.—The above acid (0.5 g.) in quinoline (10 c.c.) was refluxed on a sand bath for ½ hour with a speck of copper powder. The mixture was filtered and added to HCl (dilute) solution. The separated product was crystallised from rectified spirit in needles, m.p. 246°. (Found: C, 70.0; H, 5.6. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%).

5-Methoxy-3,8-dichloromethyl-4-methylcoumarin.—A mixture of 5-methoxy-4-methylcoumarin (1.9 g., 0.01*M*) in acetic acid (80%, 40 c.c.) and paraformaldehyde (2.4 g., 0.08*M*) was treated with HCl at 60-70° for 3 hours, and the mixture left overnight. The next day the separated solid was filtered and dried. It crystallised from benzene in needles (0.8 g.), m.p. 173-75°. (Found: C,53.9; H, 4.1; Cl, 24.6. $C_{13}H_{12}O_3Cl_2$ requires C, 54.4; H, 4.2; Cl, 24.7%).

The *diacetoxymethyl* derivative, prepared as before, crystallised from rectified spirit in needles, m.p. 168-70°. (Found: C, 61.0; H, 5.2. $C_{17}H_{18}O_7$ requires C, 61.1; H, 5.4%).

5-Methoxy-3,4,8-trimethylcoumarin.—The above dichloromethyl derivative (0.5 g.) was reduced by heating its solution in acetic acid (80 %, 20 c.c.) with zinc dust (1 g.) at 60-70° for 2 hours. The product obtained was crystallised from rectified spirit in needles, m.p. 198°. Mixed m.p. with 5-methoxy-3,4,8-trimethylcoumarin, obtained by methylation of 5-hydroxy-3, 4, 8-trimethylcoumarin, described above, in acetone solution with dimethyl sulphate in presence of anhydrous potassium carbonate as usual, was not depressed. (Found: C, 71.2; H, 6.4. $C_{13}H_{14}O_3$ requires C, 71.6; H, 6.4%).

6-*Hydroxy*-5-*chloromethyl*-4-*methylcoumarin*.—A mixture of 6-hydroxy-4-methylcoumarin (1.76g., 0.01*M*) in acetic acid (80%, 40 c.c.) and paraformaldehyde (0.3 g., 0.01*M*) was treated with HCl at 60-70° for 3 hours. The product separating on cooling was washed with ethanol and crystallised from dioxane in needles (0.8 g.), m.p. 214°. (Found : C, 59.1; H, 4.0; Cl, 15.4. $C_{11}H_9O_3Cl$ requires C, 58.8; H 4.1; Cl, 15.8%).

6-*Hydroxy*-4,5-*dimethylcoumarin*.—The above chloromethylcoumarin (0.5 g.) was heated with acetic acid (80 %, 10 c.c.) and zinc dust (1 g.) at 60-70° for 2 hours. The product separating on dilution with ice-cold water was crystallised from dilute ethanol in needles, m.p. 225°. Mixed m.p. with 6-hydroxy-3,4-dimethylcoumarin (m.p. 236°) and 6-hydroxy-4, 7-dimethylcoumarin, prepared as below (m.p. 208°), were depressed by about 20°. (Found : C, 69.3; H, 5.5. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3).

6-*Hydroxy*-4,7-*dimethylcoumarin*.—4,7-Dimethylcoumain (1 g.) was dissolved in 10% NaOH solution (40 c.c.) by warming on a steam bath. It was then oxidised with potassium persulphate (0.7 g. in 20 c.c. water) according to Parikh and Sethna (this *Journal*, 1950, **27,** 369). The product obtained was crystallised from acetic acid in needles, m.p. 208°. (Found : C, 69.5; H, 5.4. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3%) Desai and Mavani (*Proc. Ind. Acad. Sci.*, 1942, **15A,** 11), who prepared it by the Pechmann condensation of 2-methylhydroquinone and ethyl acetoacetate, reported the same m.p.

6-*Methoxy*-3,7-*dichloromethyl*-4-*methylcoumarin*.—A mixture of 6-methoxy-4-methylcoumarin (1.9 g., 0.01*M*) in glacial acetic acid (40 c.c.), paraformaldehyde (4.8 g., 0.16*M*), and anhydrous zinc chloride (2.72 g., 0.02*M*) was heated on a steam bath and dry HCl gas was passed for 3 hours. The product separating on cooling was washed with ethanol and crystallised from benzene in tiny buds (1.1 g.), m.p. 198-99°. (Found: C, 54.2; H, 4.4; Cl, 24.5. $C_{13}H_{12}O_3Cl_2$ requires C, 54.4; H, 4.2; Cl, 24.7%).

The *diacetoxymethyl* derivative, prepared as before, was crystallised from rectified spirit in needles, m.p. 162°. (Found : C, 61.2; H, 5.3. $C_{17}H_{18}O_7$ requires C, 61.1; H, 5.4%).

6-*Methoxy*-3-4,7-*trimethylcoumarin*.—The above dichloromethylcoumarin (0.5 g.) in acetic acid (80%, 10 c.c.) was heated with zinc dust (1 g.) at 60-70° for 2 hours. The product obtained crystallised from dilute acetic acid in shining needles, m.p. 159°. Mixed m.p. with 6-methoxy 3,4,7-trimethylcoumarin, obtained by methylation of 6-hydroxy-3,4,7-trimethylcoumarin which was prepared as below, was not depressed. (Found: C, 71.6; H, 6.5. $C_{13}H_{14}O_3$ requires C, 71.6; H, 6.4%).

6-*Hydroxy*-3,4,7-*trimethylcoumarin*.—3,4,7-Trimethylcoumarin was oxidised with potassium persulphate according to Parikh and Sethna (*loc. cit.*). The product obtained crystallised from acetic acid in needles, m.p. 273°. (Found: C, 70.2; H, 5.7. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%). Desai and Mavani (*loc. cit.*), who prepared it by the Pechmann condensation of 2-methylhydroquinone with ethyl ∝-methyl acetoacetate, reported m.p. 267°.

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Received August 12, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Chemistry of Aminobenzothiazoles: *N*-2-Benzothiazolylcyanamides, Related Thiocarbamides, Isothiocarbamides and Carbamides

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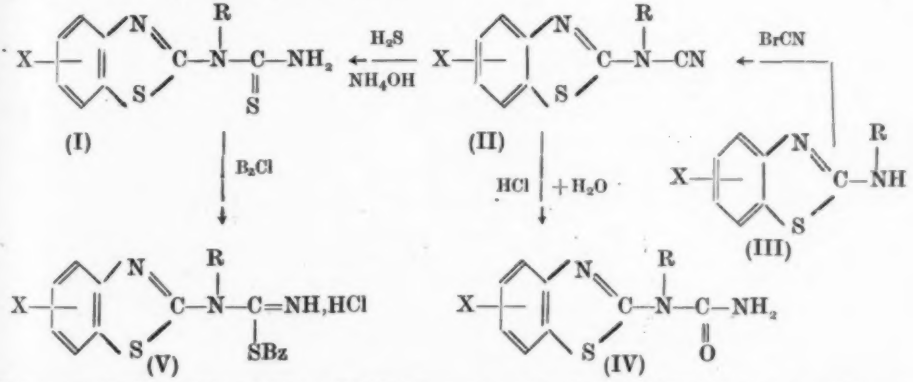
Several derivatives of thiocarbamides, cyanamides, carbamides, and isothiocarbamides containing a 2-aminobenzothiazole or substituted 2-aminobenzothiazole group, are described.

In continuation of the work reported earlier (this *Journal*, 1960, **37**, 621) the present communication describes the preparation of certain *N*-2-benzothiazolylthiocarbamides, cyanamides, and related derivatives.

Although the formation of *N*-2-benzothiazolylthiocarbamide (I) as an intermediate in the hydrochloric acid hydrolysis of phenylthiuret to 2-aminobenzothiazole had been envisaged by Fromm (*Annalen*, 1893, **275**, 20; Kurzer, *Chem. Rev.*, 1956, **56**, 154), this substance does not appear to have been prepared so far. The most obvious probable methods of obtaining it appear to be the following: (*i*) the pyrolysis of 2-aminobenzothiazole and thiocarbamide analogous to the reaction of aniline and thiocarbamide leading to phenylthiocarbamide and thiocarbanilide; (*ii*) isomerisation of 2-aminobenzothiazole thiocyanate analogous to the isomeric change of aniline thiocyanate to phenylthiocarbamide; (*iii*) interaction of 2-chlorobenzothiazole with thiocarbamide similar to the reaction of amines with the former; (*iv*) oxidative cyclisation (cf. this *Journal*, 1961, **38**, 155) of 1-phenyl-2-thio-4-*S*-benzylbiuret to *N*-2-benzothiazolyl-*S*-benzylisothiocarbamide and subsequent reduction of the latter to *N*-2-benzothiazolylthiocarbamide; (*v*) the preparation of *N*-2-benzothiazolylcyanamide (II) by the action of bromocyanogen with 2-aminobenzothiazole (III) and the thiohydrolysis of the cyanamide so obtained into *N*-2-benzothiazolylthiocarbamide (I).



(Where R is H or Me or Ph and X is Me group or hydrogen either in 3 or 6 position. Bz represents benzyl group).

The reactions (*i*) and (*ii*) under a variety of conditions afforded identical products. In the case of 2-aminobenzothiazole, this is a substance, $C_{20}H_{15}N_5S_4$, m.p. 248°, which has not been identified so far. The 3-methyl-2-iminobenzothiazole similarly gave a compound

$C_{22}H_{21}N_5S_4$, m.p. 262°. The reaction (*iii*) gave, what appears to be *S*-2-benzothiazolylisothiouronium chloride (*Proc. Ind. Sci. Cong.*, 1961, Part III, 101) and the reaction (*iv*) did not result in the expected *N*-2-benzothiazolyl-*S*-alkylisothiocarbamide, but an isomeric 5-phenylamino-3-*S*-benzyl-1,2,4-thiadiazole was formed instead. The above sequence of changes (III to I), as envisaged in (*v*), was realised though the yields were not uniformly good.

The *N*-2-benzothiazolylcyanamides (II) on hydrolysis with concentrated hydrochloric acid, as was expected, afforded the related carbamides. The *N*-2-benzothiazolylthiocarbamides on benzylation with benzyl chloride formed the related *S*-benzylisothiocarbamides (V). Several compounds of the type (I) to (V) have been prepared (*vide infra*).

EXPERIMENTAL

The required 2-aminobenzothiazoles were prepared by the oxidative cyclisation of the appropriate aryl-substituted thiocarbamides in inert solvents like benzene or chloroform (Hunter, *J. Chem. Soc.*, 1925, 2023, 2270; 1926, 3085). 2-Chlorobenzothiazole was prepared by the action of thionyl chloride on 2-mercaptobenzothiazole (cf. Suresh, *Proc. Ind. Sci. Cong.*, 1959, Part III, 134).

Mercaptobenzothiazole (50 g.) and thionyl chloride (75 c.c.) were mixed and kept without any extraneous solvent for a week at room temperature. It was then poured into excess of water and steam distilled, yielding 39.5 g. (79%) of chlorobenzothiazole, the maximum yield so far observed.

Bromocyanogen was prepared by the interaction of bromine and aqueous potassium cyanide (Scholl, *Ber.*, 1896, **29**, 1822; Williams, "Cyanogen Compounds", 1948, 2nd ed., p. 9).

(I). (*a*) *Pyrolysis of 2-Aminobenzothiazole and Thiocarbamide*

An intimate equimoleculer mixture of 2-aminobenzothiazole and thiocarbamide was heated at 160° in an oil bath for about 15 minutes; evolution of ammonia and hydrogen sulphide was noted. The product was poured into cold dilute hydrochloric acid to remove the unchanged 2-aminobenzothiazole and thiocarbamide. The residue was collected and crystallised from solvents like glacial acetic acid and chlorobenzene; m.p. 248°. It is nondesulphurisable with sodium plumbite solution. (Found: C, 53.69; H, 3.03; N, 15.36; S, 27.82. $C_{21}H_{15}N_5S_4$ requires C, 52.98; H, 3.31; N, 15.45; S, 28.25%).

(*b*) *Pyrolysis of 2-Aminobenzothiazole Thiocyanate.*—On mixing concentrated aqueous solutions of 2-aminobenzothiazole hydrochloride and ammonium thiocyanate, 2-aminobenzothiazole thiocyanate was obtained as a white precipitate, m.p. 168°. It was heated at its m.p. for about one hour and poured into excess of cold water. The solid collected was crystallised from acetic acid, m.p. 248°. (Found: N, 15.35; S, 27.85. $C_{20}H_{15}N_5S_4$ requires N, 15.45; S, 28.25%). It was found to be identical with the product obtained by the pyrolysis of 2-aminobenzothiazole and thiocarbamide.

(*c*) *Pyrolysis of 3-Methyl-2-iminobenzothiazole and Thiocarbamide.*—An intimate mixture of 3-methyl-2-iminobenzothiazole and thiocarbamide was heated at 160° for about 20-25 minutes. The mixture was poured into HCl (cold, dilute) to remove the

unchanged reactants. The solid residue was collected and crystallised from absolute ethanol and acetic acid, m.p. 262°. It was not desulphurisable with sodium plumbite solution. (Found: C, 54.76; H, 3.96; N, 14.04; S, 26.1. $C_{23}H_{21}N_5S_4$ requires C, 55.75; H, 4.24; N; 14.14; S, 25.85%).

(*d*) *Pyrolysis of 3-Methyl-2-iminobenzothiazole Thiocyanate.*—3-Methyl-2-iminobenzothiazole thiocyanate was prepared by mixing aqueous solutions of 3-methyl-2-iminobenzothiazole hydrochloride and ammonium thiocyanate; m.p. 178°. It was heated at 130-40° for about 2 hours. The product was poured into excess of cold water and the solid product was collected and crystallised from ethanol, m.p. 262°. (Found: N, 14.09; S, 26%). It is identical with the product obtained in (*c*).

(II). *Interaction of 2-Chlorobenzothiazole with Thiocarbamide*

An intimate mixture of 2-chlorobenzothiazole and thiocarbamide was heated at 30-40° for about 1 hour. The pasty mass obtained was washed with dry acetone to remove the unchanged reactants. The residue left was found to be acidic; m.p. 158°. It decomposed in contact with water yielding 2-mercaptobenzothiazole, cyanamide, and carbamide. It gave a picrate, m.p. 172°. (Found: C, 39.6; H, 3.13; N, 16.83; S, 26.74. $C_8H_8N_3ClS_2$ requires C, 39.1; H,3.25; N, 1; 17.S, 26.06%). Equivalent weight of the hydrochloride was found titrimetrically. (Found: Equiv., 243.3. $C_8H_8N_3S_2Cl$ requires equiv., 245.5).

This substance was identified as *S*-2-benzothiazolylisothiouronium chloride. The same product was obtained by refluxing an equimolecular mixture of 2-chlorobenzothiazole and thiocarbamide in dry acetone for about 15 minutes.

(III). *Oxidation of 1-Phenyl-2-thio-4-S-benzylbiuret in Benzene with Bromine*

1-Phenyl-2-thio-4-*S*-benzylbiuret was prepared by heating a mixture of *S*-benzylisothiouronium chloride and phenyl isothiocyanate for half-an-hour and by subsequent basification of the product; m.p. 116°. (Found: N, 13.88. $C_{15}H_{15}N_3S_2$ requires N, 13.95%). Hydrochloride, m.p. 165°. (Found: Equiv., 339.8. $C_{15}H_{15}N_3S_2$, HCl requires equiv., 337.5).

A clear solution of this isodithiobiuret was taken in benzene and molecular bromine was added till the colour of bromine persisted. The solid product thus obtained was filtered, dissolved in water, and basified. The base was crystallised from ethanol, m.p. 154°. (Found: N, 13.68; S, 21.52. $C_{15}H_{13}N_3S_2$ requires N,14.04; S, 21.4%).

On reduction with hydrogen sulphide in presence of aqueous or ethanolic ammonia shining yellow crystals were obtained which on crystallisation fromm ethanol melted at 185°. This was identified with 1-phenyldithiobiuret (From m *et al.*, *Annalen*, 1893, **275**, 34). The original product could not therefore be a benzothiazolyl derivative.

(IV). N-2-*Benzothiazolylcyanamide*

Dilute ethereal solutions of the appropriate 2-aminobenzothiazole and half the molecular quantity of bromocyanogen were mixed and kept for 1 to 2 hours at 40-60°. Reaction proceeded with the separation of the hydrobromide of the starting aminobenzo-

thiazole. The cyanamide formed was retained in the ethereal solution and was separated from the hydrobromide by filtration, followed by evaporation of the ether. Thus was obtained a mixture of unchanged aminobenzothiazole and its cyanamide. In the case of 2-benzothiazolyl- and 2-(6-methyl)benzothiazolyl-cyanamides, separation of the pure cyanamide was effected by extraction with alkali in which these were soluble and could be reprecipitated by just acidification.

The 3-methyl-2-benzothiazolyl cyanamide is not very soluble in ether. It was precipitated along with the hydrobromide; so the cyanamide was separated by washing the unchanged aminobenzothiazole and its hydrobromide with cold dilute acid.

6-Methyl-2-methylaminobenzothiazole afforded a cyanamide which was dimorphous. One form is soluble in ether and the other insoluble.

Cyanamides were prepared from the following aminobenzothiazoles: (*i*) 2-amino-, (*ii*) 6-methyl-2-amino-, (*iii*) 3-methyl-2-imino-, (*iv*) 2-methylamino-, (*v*) 6-methyl-2-methylamino-, (*vi*) 2-phenylamino-. These were crystallised from absolute ethanol and chlorobenzene. The physical characteristics and results of analyses are recorded in Table I.

N-2-Benzothiazolylthiocarbamides.—The *N*-2-benzothiazolylcyanamides, obtained above, were treated with ethanolic ammonium hydrogen sulphide solution and the mixture was boiled for about 20 to 30 minutes. The cyanamides first went into solution; on continued boiling the related thiocarbamides were precipitated. These were collected after cooling the reaction mixture and crystallised from solvents like absolute ethanol and chlorobenzene in shining crystals. All the cyanamides except 3-methyl-2-benzothiazolylcyanamide could be thiohydrolised into the related thiocarbamides. All the thiocarbamides were desulphurizable with sodium plumbite solution. *N*-2-benzothiazolyl-, and *N*-2-(6-methyl)benzothiazolyl-thiocarbamides were found soluble in cold alkali and to precipitate the corresponding cyanamides on acidification. All the thiocarbamides melted with decomposition with evolution of hydrogen sulphide. Their physical characteristics and results of analyses are summarised in Table II.

N-2-*Benzothiazolyl*-S-*benzylisothiocarbamides.* — *N*-2-benzothiazolylthiocarbamides and benzyl chloride in equimolecular proportion were refluxed in absolute ethanol for 30 to 40 minutes. The clear solution on cooling threw out crystals of the related isothiouronium chlorides. Equivalent weights of these hydrochlorides were determined titrimetrically. Free bases were prepared and crystallised from dilute ethanol. Analyses, physical characteristics and equivalent weights are recorded in Table III.

N-2-*Benzothiazolylcarbamides.*—The cyanamide (1g.) and HCl (conc., 20 c.c.) were boiled under reflux for about 1 hour. The cyanamide dissolved at first forming a clear solution; on continued boiling a white fluffy precipitate was thrown out. On filtration and crystallisation from acetic acid, needle-shaped crystals were obtained. These were the related carbamides. The results of these experiments are summarised in Table IV.

In the case of 2-amino-, 2-amino-(6-methyl)-, and 3-methyl-2-iminobenzothiazoles, the corresponding carbamides were also obtained by heating these benzothiazoles with carbamide at 130-40° for 5 to 10 minutes. These were found to melt at 300°, 408°, and

TABLE I

N-2-*Benzothiazolylcyanamides.*

No.	Reactants.	Solvent.	Cyanamide formed. (Yield).	Colour.	Formula.	Cryst. from.	M.P.	Found.	Calc.	Remarks.
1.	2-Amino-BT† +BrCN	Ether (Sulphuric)	*N*-2-BT-cyanamide (30%)	White	$C_8H_5N_3S$	Absolute ethanol	181°	C : 55.15% H : 2.85 N : 23.93 S : 18.42	54.85% 2.85 24.00 18.28	Soluble in alkali & acid. Titratable against alkali. Equiv. found, 179.3. $C_8H_5N_3S$ requires equiv., 175.
2.	2-Amino-(6-methyl)-BT+BrCN	Do	*N*-2-(6-Methyl)-BT-cyanamide (35%)	,,	$C_9H_7N_3S$	,,	193°	C : 56.96 H : 3.96 N : 21.89 S : 17.24	57.14 3.70 22.22 16.93	Soluble in alkali & acid. Titratable against alkali. Equiv. found, 192.4; $C_9H_7N_3S$ reuires equiv. 189.
3.	3-Methyl-2-imino-BT +BrCN	Ether-benzene mixture	*N*-2-(3-Methyl)-BT-cyanamide (80-90%)	Greenish yellow	$C_9H_7N_3S$	Bezene-ethanol mixture	175°	C : 57.00 H : 3.58 N : 21.85 S : 16.73	57.14 3.70 22.22 16.93	Insoluble in alkali and acid.
4.	2-Methyl-amino-BT +BrCN	Ether	*N*-2-(*N*-Methyl)-BT-cyanamide (80-90%)	White	$C_9H_7N_3S$	Absolute ethanol	102°	C : 57.31 H : 3.73 N : 21.89 S : 16.83	57.14 3.70 22.22 16.93	Do
5.	2-Methyl-amino-(6-methyl)-BT+BrCN	Ether	N-2-(*N*-Methyl)-(6-methyl)-BT-cyanamide (60-65%) (ether soluble)	,,	$C_{10}H_9N_3S$	,,	*104°	C : 59.49 H : 4.69 N : 20.38 S : 16.02	59.11 4.40 20.68 15.76	,,
6.	Do	,,	Do (ether insoluble) (20%)	Yellow	$C_{10}H_9N_3S$	Chloro-benzene	*168°	N : 20.76 S : 15.91	20.68 15.76	
7.	2-Phenyl-amino-BT +BrCN	Benzene	*N*-2-(*N*-Phenyl)-BT-cyanamide (90%)	White	$C_{14}H_9N_3S$	Absolute ethanol	132°	C : 66.99 H : 3.64 N : 16.54 S : 12.58	66.93 3.58 16.73 12.74	,,

† BT represents benzothiazole.

* Dimorphous forms of the cyanamide.

TABLE II

N-2-*Benzothiazolylthiocarbamides.*

S. No.	Cyanamide thio-hydrolysed.	Thiocarbamide formed (yield).	Colour.	Formula.	Cryst.from.	M.P.	Found.	Calc.	Remarks.
1.	N-2-BT-cyanamide	*N*-2-BT-thiocarbamide (80%)	Yellow	$C_8H_7N_3S_2$	Absolute ethanol	209°	C : 46.21% H: 3.63 N: 20.08 S : 30.94	45.93% 3.39 20.09 30.62	Soluble in cold alkali; cyanamide precipitated on neutralisation.
2.	N-2-(6-Methyl)-BT-cyanamide	*N*-2-(6-Methyl)BT-thiocarbamide (80%)	White	$C_9H_9N_3S_2$	Do	212°	C : 48.39 H : 4.68 N : 18.72 S : 28.89	48.43 4.03 18.83 28.69	Soluble in cold alkali; cyanamide precipitated on neutralisation.
3.	*N*-2-(*N*-Methyl)-BT-cyanamide.	*N*-2-(*N*-Methyl)-BT-thiocarbamide (80-90%)	,,	$C_9H_9N_3S_2$	Chloro-benzene	156°	C : 48.49 H : 4.35 N : 18.72 S : 28.41	48.43 4.03 18.83 28.69	Insoluble in cold alkali.
4.	*N*-2-(6-Methyl-*N*-methyl)-BT-cyanamide (104°)	*N*-2-(6-Methyl-*N*-methyl)-BT-thiocarbamide (75-80%)	Faint yellow	$C_{10}H_{11}N_3S_2$	Do	*181°	C : 50.86 H : 4.78 N : 17.81 S : 27.24	50.63 4.64 17.72 27.00	Do; mixed m.p. of 181° and 199° did not show any depression.
5.	Do (168°)	Do	Deep yellow	$C_{10}H_{11}N_3S_2$	,,	*199°	N : 17.70 S : 27.12	17.72 27.00	
6.	*N*-2-(*N*-Phenyl)-BT-cyanamide.	*N*-2-(*N*-Phenyl)-BT-thiocarbamide	White	$C_{14}H_{11}N_3S_2$	Ethanol	138°	N: 14.64 S : 22.59	14.74 22.45	Insoluble in cold alkali.

* The thiocarbamides are dimorphous.
BT represents benzothiazolyl.

TABLE III

N-2-*Benzothiazolyl*-S-*benzylisothiouronium chlorides.*

No.	Reactants.	Isothiouronium chloride.	M.P.	Equivalent weight. Found.	Equivalent weight. Calc.	Free base m.p.	Found.	Calc.
1.	*N*-2-BT-thiocarbamide + BzCl	*N*-2-BT-*S*-benzyliso-T ($C_{15}H_{13}N_3S_2$.HCl)	212°	337.8	335.5	78° ($C_{15}H_{13}N_3S_2$)	C : 59.95% H : 4.35 N : 13.87	60.20% 4.34 14.04
2.	*N*-2-(6-Methyl)-BT-thiocarbamide + BzCl	*N*-2-(6-Methyl)-BT-*S*-benzyliso-T ($C_{16}H_{15}N_3S_2$.HCl)	201°	352.2	349.5	118° ($C_{16}H_{15}N_3S_2$)	C : 61.17 H : 4.77 N : 13.12	61.34 4.79 13.41
3.	*N*-2-(*N*-Methyl)-BT-thiocarbamide + BzCl	*N*-2-(*N*-Methyl)-BT-*S*-benzyliso-T ($C_{16}H_{15}N_3S_2$.HCl)	235°	348.7	349.5	71° ($C_{16}H_{15}N_3S_2$)	C : 61.66 H : 4.84 N : 13.48	61.34 4.79 13.41
4.	*N*-2-(*N*-Methyl-6-methyl)-BT-thiocarbamide + BzCl	*N*-2-(*N*-Methyl-6-methyl)-BT-*S*-benzyliso-T ($C_{17}H_{17}N_3S_2$.HCl)	242°	365.3	363.5	155° ($C_{17}H_{17}N_3S_2$)	N : 13.09	12.84
5.	*N*-2-(*N*-Phenyl)-BT-thiocarbamide + BzCl	*N*-2-(*N*-Phenyl)-BT-*S*-Benzyliso-T ($C_{21}H_{17}N_3S_2$HCl)	150°	408.5	411.5	139° ($C_{21}H_{17}N_3S_2$)	N : 11.15	11.2

BzCl represents benzyl chloride.

BT represents benzothiazolyl.

T „ thiouronium chloride.

TABLE IV

N-2-*Benzothiazolylcarbamides*.

Cyanamide hydrolysed.	Carbamide formed.	Colour.	Cryst. from.	M.P.	Found.	Calc.
1. *N*-2-Benzothiazolylcyanamide	*N*-2-Benzothiazolylcarbamide. ($C_8H_7ON_3S$)	White	Gl. acetic acid.	*300°		
2. *N*-2-(6-Methyl)benzothiazolyl-cyanamide	*N*-2-(6-Methyl) benzothiazolyl-carbemide ($C_9H_9ON_3S$)	,,	Do	*308°		
3. *N*-2-(3-methyl)benzothiazolyl-cyanamide	*N*-2-(3-Methyl)benzothiazolyl-carbamide ($C_9H_9ON_3S$)	Greenish yellow	Chlorobenzene	230°	N : 20.05 S : 15.61	20.28 15.45
4. *N*-2-Benzothiazolyl-*N*-methyl-cyanamide	*N*-2-Benzothiazolyl-*N*-methyl-carbamide ($C_9H_9ON_3S$)	White	Do	187°	N : 20.12	20.28
5. *N*-2-(6-Methyl)benzothiazolyl-*N*-methylcyanamide	*N*-2-(6-Methyl)benzothiazolyl-*N*-methylcarbamide ($C_{10}H_{11}ON_3S$)	,,	Gl. acetic acid	234°	N : 18.96	19.00
6. *N*-2-Benzothiazolyl-*N*-phenyl-cyanamide	*N*-2-Benzothiazolyl-*N*-phenyl-carbamide ($C_{14}H_{11}ON_3S$)	,,	Do	156°	N : 15.58	15.61

*Joshua, *this Journal* 1960, **37**, 621.

230° respectively. These were identical with those obtained by hydrolysis of the related cyanamides (vide Table IV).

Sincere thanks of the author are due to Dr. R. H. Sahasrabudhey for his interest, to Dr. G. B. Singh, Head of the Department of Chemistry, and the authorities of the Banaras Hindu University for the facilities and to the University Grants Commission for a research scholarship.

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Received May 27, 1961.

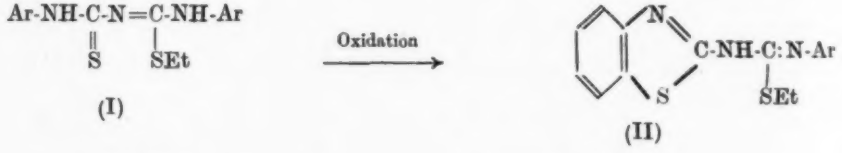
[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Oxidative Debenzylation and Cyclisation of 1-Aryl-or-alkyl-4-*S*-benzyliso-2,4-dithiobiurets: Formation of *S*-Aryl or alkylamino-3-imino-1,2,4-dithiazolidines or/and the Related 1,2,4-Thiadiazoles

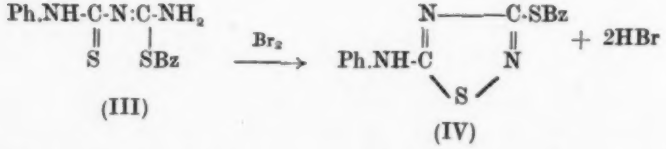
C. P. Joshua and V. K. Verma

Depending on the nature of the solvent and the concentration of the reactants, the oxidation of 1-aryl or alkyl-4-*S*-benzyliso-2,4-dithiobiurets is shown to afford either the 5-aryl or alkylamino-3-imino-1,2,4-dithiazolidines or the related 1,2,4-thiadiazoles.

1, 5-Diaryl-2-*S*-ethyliso-2,4-dithiobiurets (I), when oxidised with bromine or iodine, have been found to undergo ring closures to *N*-2-benzothiazolyl-*N'*-aryl-*S*-ethylisothiocarbamides (II) (Joshua, this *Journal*, 1961, **38**, 155). On the other hand, Kurzer and Taylor (*J. Chem. Soc.*, 1959, 1064) have reported the formation (in 45% yield) of 5-phenylamino-3-*S*-benzyl-1,2,4-thiadiazole (IV) by oxidation by bromine of 1-phenyl-4-*S*-benzyliso-2,4-dithiobiuret(III) in chloroform.



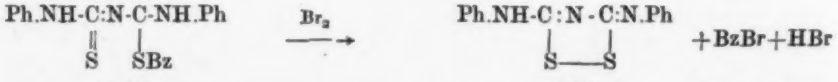
(I) (II)



(III) (IV)

Since the reported yield of (IV) was not satistactory, the reaction leading to it probably was not the only reaction taking place (Kurzer and Taylor, *loc. cit.*, p. 1066). The differing modes of ring closure observed as above could be due to the difference in the nature of the substituents in positions 1,4, and 5, or due to the change in the working conditions, or both.

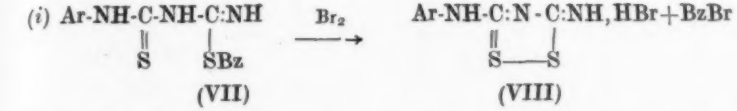
In view of these facts and also in the light of the oxidation by bromine of 1,5-diphenyl-2-*S*-benzyliso-2,4-dithiobiuret (V) to 5-phenylamino-3-phenylimino-1,2,4-dithiazolidine (VI), observed in these laboratories, a reinvestigation of the oxidations generally and interaction of bromine, especially with the above dithiobiurets, has been carried out.



(V) (VI)

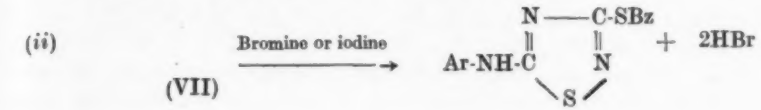
The present communication describes the results obtained with 1-phenyl-, 1-*p*-tolyl-, 1-*m*-tolyl-, 1-*m*-xylyl-, 1-methyl-, 1-ethyl-, and 1-propyl[n]-4-*S*-benzyliso-2,4-dithiobiurets.

Bromine in concentrated solutions in chloroform or benzene was found to afford the hydrobromides of the related 5-aryl- or -alkylamino-3-imino-1,2,4-dithiazolidines. This reaction can be represented as:



(VII) (VIII)

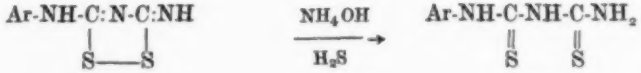
In dilute solutions of the above reactants in the same solvents or in ethanolic solutions with bromine or iodine, another reaction (*ii*) took place when the principal product was 5-aryl- or -alkylamino-3-*S*-benzyl-1,2,4-thiadiazole (IX).



(IX)

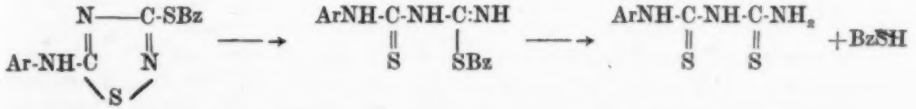
The reaction (*ii*) also took place to a small extent in concentrated chloroform or benzene solutions. Thus concentration of the reactants, especially the strength of the oxidant, appears to be the deciding factor whether the reaction would procee along the route (*i*) or (*ii*).

The dithiazolidine (VIII) on reduction with alkaline sulphide easily afforded the related dithiobiuret (X).



(VIII) (X)

The thiadiazoles (IX) also on similar reduction gave the dithiobiurets (X). In the case of 5-methyl-3-*S*-benzyl-1,2,4-thiadiazole, 1-methyl-4-*S*-benzyliso-2,4-dithiobiuret was obtained as the initial reduction product; this on prolonged reduction afforded the 1-methyl-2,4-dithiobiuret which suggested the following sequence of changes (cf. Kurzer and Taylor, *loc. cit.*, p, 1067):



This was in agreement with earlier observed facts (Curd *et al.*, *J. Chem. Soc.*, 1949, 740) and our own unpublished work on reductive debenzylation by alkaline sulphide, that debenzylation or dealkylation was not effected when there was no hydrogen on the adjoining nitrogen atoms.

In no case was a benzothiazolyl derivative obtained. The main experimental results have been summarised in Tables I to IV. In all the cases the identification of the products was carried out with authentic samples prepared by alternative methods.

EXPERIMENTAL

1-*Alkyl- or -aryl*-4-S-*benzyliso*-2,4-*dithiobiurets* were readily obtained by condensing the corresponding isothiocyanate with *S*-benzylisothiouronium base. Details of a typical experiment leading to the formation of 1-phenyl-4-*S*-benzyliso-2,4-dithiobiuret are shown below.

S-Benzylisothiouronium chloride was mixed with an equimolecular quantity of phenylisothiocyanate and the required quantity of a 10% solution of alkali was added to neutralise the hydrochloride. The pasty mass so obtained was warmed for 10 minutes on a water bath and extracted with benzene. Benzene extract was heated under reflux for 20 to 30 minutes, solvent removed, and the residual semisolid treated with HCl (conc.) when the hydrochloride of the isodithiobiuret was obtained. It was freed of the unchanged reactants by washing with ether and cold water. The salt on basification afforded 1-phenyl-4-*S*-benzyliso-2, 4-dithiobiuret, crystallised from ethanol as white needles. The other 1-aryl- and -alkylisodithiobiurets were prepared similarly.

The *S*-benzylisothiouronium chloride and the isothiocyanates also condensed directly when heated on a water bath under reflux for about 2 hours, affording the corresponding isodithiobiuret hydrochlorides in good yields. Physical characteristics and the other data about the respective isodithiobiurets are recorded in Table I.

Oxidation of 1-*Aryl- or* 1-*Alkyl*-4-S-*benzyliso*-2,4-*dithiobiurets*

(*a*) *With Bromine in Chloroform.*—The required isodithiobiuret was dissolved in minimum quantity of warm chloroform and bromine was added with good stirring. A yellowish crystalline solid separated with evolution of lachrymatic fumes of benzyl bromide. The solid was filtered, washed with ether, and dried. Crystallisation from ethanol in presence of a little hydrobromic acid afforded crystalline products. These were the hydrobromides of the related 5-substituted amino-3-imino-1,2,4-thiadiazolidines. All the isodithiobiurets were oxidised in a similar manner. Results are summarised in Table II.

Oxidation of the isodithiobiurets in benzene and carbon tetrachloride also afforded the same products provided that the concentration of the substance in the solvent was very high and pure liquid bromine used as oxidant. With higher dilution of the solvent the dithiazolidine and the 1,2,4-thiadiazole were formed in different proportions depending on the degree of dilution of the reactants. The two products could be separated by fractional crystallisation from ethanol. The more soluble one on treatment with alkali liberated a free base which was identified as the 1,2,4-thiadiazole. The sparingly ethanol-soluble part was soluble in alkali and identified as the corresponding dithiazolidine hydrobromide (Table II).

(*b*) *With Bromine in Ethanol.*—To an ethanolic solution of the isodithiobiuret was added a dilute ethanolic solution of bromine till the colour of bromine persisted. The solution was stirred into excess of cold water and basified when a white solid separated. On

TABLE I

TABLE I

1-Aryl or alkyl-4-S-benzyliso-2,4-dithiobiurets.

No.	Reactants.	1-Substituted-4-*S*-benzyliso-2,4-dithiobiurets formed.	Cryst. from.	M.P.	Hydrochloride. M.P.	Equiv. wt. Found.	Equiv. wt. Calc.	Found.	Calc.
1.	Phenyl-I-SB.-T.C.	•1-Phenyl- ($C_{15}H_{15}N_3S_2$)	Ethanol	116°	165°	334.2 ($C_{15}H_{15}N_3S_2$,HCl)	337.5	N : 13.68%	13.95%
2.	*p*-Tolyl-I-SB.-T.C.	1-*p*-Tolyl- ($C_{16}H_{17}N_3S_2$)	Methanol	120°	163°	347.2 ($C_{16}H_{17}N_3S_2$,HCl)	351.5	C : 60.65 H : 5.29 N : 13.42	60.95 5.39 13.33
3.	*m*-Tolyl-I-SB.-T.C.	1-*m*-Tolyl- ($C_{16}H_{17}N_3S_2$)	Ethanol	101°	162°	348.3 ($C_{16}H_{17}N_3S_2$,HCl)	351.5	N : 13.32	13.33
4.	*m*-Xylyl-I-SB.-T.C.	1-*m*-Xylyl- ($C_{17}H_{19}N_3S_2$)	Do	116°	164°	359.9 ($C_{17}H_{19}N_3S_2$,HCl)	365.5	N : 12.76	12.79
5.	Methyl-I-SB.-TC.	•1-Methyl- ($C_{10}H_{13}N_3S_2$)	Do (75%)	97°	167°	275.8 ($C_{10}H_{13}N_3S_2$,HCl)	275.5	N : 17.30	17.57
6.	Ethyl-I-SB.-TC.	1-Ethyl- ($C_{11}H_{15}N_3S_2$)	Methanol	72°	171°	285.3 ($C_{11}H_{15}N_3S_2$,HCl)	289.5	N : 16.82	16.60
7.	Propyl^n-I-SB.-T.C.	•1-Propyl^n- ($C_{12}H_{17}N_3S_2$)		Liquid at room temp.	180°	291.8 ($C_{12}H_{17}N_3S_2$,HCl)	303.4		

•Kurzer and Taylor (*J. Chem. Soc.*, 1959, 1064).

I represents isothiocyanate.

T.C. represents isothiouronium chloride.

SB. represents *S*-benzyl.

crystallisation from ethanol colorless, needle-shaped crystals of the related 1,2,4-thiadiazoles were obtained.

TABLE II

Oxidation of 1-aryl-or-alkyl-4-S-benzyliso-2,4-dithiobiurets by bromine.

No.	Isodithiobiuret oxidised.	Solvent.	1,2,4-Dithiazolidine formed.	Yield.	M.P.	**Authentic sample m. p.	Mixed m. p.
1.	1-Phenyl-4-SB- ($C_{15}H_{15}N_3S_2$)	Chloroform	5-Phenylamino-3-imino- ($C_8H_7N_3S_2$,HBr)	90%	210°	210°	210°
2.	1-*p*-Tolyl-4-SB- ($C_{16}H_{17}N_3S_2$)	,, ,,	5-*p*-Tolylamino-3-imino- ($C_9H_9N_3S_2$,HBr)	90	222°	220°	221°
3.	1-*m*-Tolyl-4-SB- ($C_{16}H_{17}N_3S_2$)	,, ,,	5-*m*-Tolylamino-3-imino- ($C_9H_9N_3S_2$,HBr)*	80	205°	205°	205°
4.	1-*m*-Xylyl-4-SB- ($C_{17}H_{19}N_3S_2$)	Benzene	5-*m*-Xylylamino-3-imino- ($C_{10}H_{11}N_3S_2$,HBr)*	80-85	165°	163°	165°
5.	1-Methyl-4-SB- ($C_{10}H_{13}N_3S_2$)	,,	5-Methylamino-3-imino- ($C_3H_5N_3S_2$,HBr)*	80	225°	228°	226°
6.	1-Ethyl-4-SB- ($C_{11}H_{15}N_3S_2$)	,,	5-Ethylamino-3-imino- ($C_4H_7N_3S_2$, HBr)	80-85	152°	154°	154°
7.	1-Propyl^n-4-SB- ($C_{12}H_{17}N_3S_2$)	CCl_4	5-Propyl^n amino-3-imino- ($C_5H_9N_3S_2$,HBr)*	80	160°	162°	162°

*In these cases the related thiadiazoles were obtained in small quantities (about 10% yield).

The hydrobromides of the dithiazolidines were obtained by oxidation of authentic dithiobiuret samples (Fromm *et al.*, *Annalen*, 1893, 1893, **275, 34; Dixit, *this Journal*. 1961, **38**, 44).

(*c*) *With Iodine in Ethanol.*—To a clear solution of the isodithiobiuret in ethanol was added an ethanolic solution of iodine till no further decolorisation took place. Treatment of the solution with an excess of water precipitated a solid product. It was collected and crystallised from ethanol. In every case the product was identical with the related 1,2,4-thiadiazole (*vide supra*). The results of these oxidations are presented in Table III.

The oxidation products obtained by the procedure (*a*) were identified as the hydrobromides of 5-aryl-or-alkylamino-3-imino-1,2,4-dithiazolidines. These were also obtained by oxidation of the corresponding dithiobiurets, which were prepared by the action of amines on isopersulphocyanic acid (Fromm *et al.*, *Annalen*, 1893, **275**, 34; 1908, **361**, 319; Dixit, this *Journal*, 1960, **38**, 44).

Reduction of 1-Alkyl-or-arylamino-3-S-benzyl-1,2,4-thiadiazoles with Ammoniacal Hydrogen Sulphide.—The thiadiazoles on shaking with a solution of ammonium hydrogen sulphide in ethanol went into solution and the related dithiobiurets were thrown out after

standing for about an hour or on acidification. The product was collected and crystallised from ethanol. In some cases the reduction took place only after passing hydrogen sulphide through warm ammoniacal solution for about an hour. In the case of 5-methylamino-3-*S*-benzyl-1,2,4-thiadiazole, the related 1-methyl-4-benzyliso-2,4-dithiobiuret was obtained as the initial reduction product, which on further reduction afforded the dithiobiuret. The dithiobiurets were identified by comparison with authentic samples prepared by the reaction of isopersulphocyanic acid and the amines (*loc. cit.*).

TABLE III

Oxidation of isodithiobiurets by bromine or iodine in ethanol.

No.	4-*S*-Benzyliso-2, 4-dithiobiurets oxidised.	3-*S*-Benzyliso-1,2,4-thiadiazole formed.	Cryst. from.	M.P.	Found.	Calc.
1.	1-Phenyl-	5-Phenylamino-* ($C_{15}H_{13}N_3S_2$)	Ethanol	154°	N : 14.1%	14.04%
2.	1-*p*-Tolyl-	5-*p*-Tolylamino- ($C_{16}H_{15}N_3S_2$)	,,	173°	C : 61.66 H : 4.84 N : 13.39	61.34 4.79 13.41
3.	1-*m*-Tolyl-	5-*m*-Tolylamino- ($C_{16}H_{15}N_3S_2$)	Methanol	86°	N : 13.28	13.41
4.	1-*m*-Xylyl-	5-*m*-Xylylamino- ($C_{17}H_{17}N_3S_2$)	Ethanol	163°	N : 12.62	12.84
5.	1-Methyl-	5-Methylamino-* ($C_{10}H_{11}N_3S_2$)	Methanol	137°	C : 50.45 H : 4.46 N : 17.96	50.63 4.46 17.72
6.	1-Ethyl-	5-Ethylamino- ($C_{11}H_{13}N_3S_2$)	,,	67°	N : 16.60	16.73
7.	1-Propyl-	5-Propyl- amino-* ($C_{12}H_{15}N_3S_2$)	,,	92°	N : 15.96	15.84

*Kurzer and Taylor, *loc. cit*,.

Reduction of 5-Alkyl- or -arylamino-3-imino-1,2,4-dithiazolidine Hydrobromides with Ammonium Hydrogen Sulphide.—The 5-alkyl- or -arylamino-3-imino-1,2,4-dithiazolidines obtained in the oxidation of 1-aryl- or -alkyl-4-*S*-benzyliso-2,4-dithiobiurets (Table II) were dissolved in ethanolic ammonium hydrogen sulphide and hydrogen sulphide passed for 10 to 15 minutes. The reaction mixture after acidification was filtered. The residue on crystallisation from ethanol or water afforded crystals of the corresponding dithiobiurets, identified by undepressed mixed melting points with authentic samples. The results are summarised in Table IV.

TABLE IV

Reduction of the oxidation products of the isodithiobiurets.

No.	Oxidation products reduced,	Dithiobiurets. formed.	Cryst from.	M.P.	Authentic sample m.p.	Mixed m.p.
1.	(*a*) 5-Phenylamino-T	1-Phenyl-	Ethanol	184°	**179°	182°
	(*b*) 4- ,, DA	,,		178°	179°	179°
2.	(a) 5-*p*-Tolylamino-T	1-*p*-Tolyl-	,,	173°	**173°	173°
	(b) 5-*p*- ,, DA	,,		171°	173°	172°
3.	(a) 5-*m*-Tolylamino-T	1-*m*-Tolyl-	Methanol	158°	158°	158°
	(b) 5-*m*- ,, DA	,,		156°	158°	158°
4.	(a) 5-*m*-Xylylamino-T	1-*m*-Xylyl-	Ethanol	120°	121°	121°
	(b) 5-*m*- ,, DA	,,		120°	121°	121°
5.	(a) 5-Methylamino-T	1-Methyl-	Water	153°	*153°	153°
	(b) 5- ,, DA	,,		152°	153°	153°
6.	(a) 5-Ethylamino-T	1-Ethyl-	,,	175°	*176°	176°
	(b) 5- ,, DA	,,		175°	176°	176°
7.	(a) 5-Propyl^n amino-T	1-Propyl^n	Ethanol (25%)	120°	*121°	121°
	(b) 5- ,, DA	,,		121°	121°	121°

Fromm *et al.*, *Annalen*, 1893, **275, 34; 1908, **361**, 319.
*Dixit, *this Journal*, 1961, **38**, 44.
T represents 3-*S*-benzyl-1,2,4-thiadiazole.
DA represents 3-iminodithiazolidine.

Sincere thanks of the authors are due to Dr. R. H. Sahasrabudhey for his kind interest, to Professor G. B. Singh and to the authorities of the Banaras Hindu University for facilities, and to the University Grants Commission and the Council of Scientific and Industrial Research for scholarships to C.P.J. and V.K.V. respectively.

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Received August 8, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Effect of Nature and Concentration of Supporting Electrolyte on the Half-wave Potential and Diffusion Current. Part I

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Influence of variation of the nature and concentration of the supporting electrolyte on the half-wave potential and diffusion current of Cd^{2+} and Zn^{2+} as reducing ions has been studied. An attempt has been made to correlate these data (specially those of the diffusion current) with viscosity, but such a correlation has been found to be not always possible. In some cases the possibility of complex formation is suggested.

In a previous communication (Mukherjee *et al.*, *J. Sci. Ind. Res.*, 1961, **20B**, 77) it has been shown that there has been decrease both in the half-wave potential and in the diffusion current when the viscosity of the solution is increased gradually by addition of glycerin to the medium containing 0.1*M*-KCl as a supporting electrolyte and $1 \times 10^{-3}M$ of the reducible ions, Cd^{2+} and Zn^{2+}. The diffusion current was, however, found to vary linearly with the square root of D, the diffusion coefficient. This signifies that $i_d\eta^{\frac{1}{2}}$ is expected to be constant in such cases. It is therefore concluded that mere change in the viscosity of the medium has no other singnificant complicating influence and obeys Ilkovic's equation in a regular manner.

In the present series of communications, it is our object to study the influence of variation of the nature and concentration of the supporting electrolyte on these two parameters and to examine whether any complicating factors arise in such cases.

EXPERIMENTAL

The present study is confined to the cases of the reducing ions Cd^{2+} and Zn^{2+} only, with the supporting electrolytes: KCl, KNO_3, NH_4Cl, HCl. Chemicals used were all of G.R. quality of E.Merck. The instrument was found to yield $E_{\frac{1}{2}}$ within ± 0.005 volts and i_d within ± 0.125 μa. The drop time was about 3 secs. and the mass flow rate for mercury was 1.6 to 1.8 mg. per second. Purified nitrogen gas was passed through the solution for about 15 to 20 minutes to get rid of the dissolved oxygen. Gelatine (0.005%) was used as a suppressor in every case. $E_{\frac{1}{2}}$ was measured against the saturated calomel electrode.

Viscosity was measured relative to that of water by an Ostwald viscometer* at a constant temperature (accurate to $\pm 0.05°$). The mean flow time of water through the capillary (based on 10 readings) was 132.95 ± 0.1 sec. Each of the viscosity readings shown here represents the mean of at least five different observations. Results are shown in Tables I and II.

*British Standard U-tube type with N.P.L. certificate.

TABLE I

Cd^{2+} *as the reducing ion.*

Supporting electrolyte conc.	i_d(μa).	$E_{\frac{1}{2}}$ (volts).	Viscosity (η).	$i_d\eta^{\frac{1}{2}}$.	i_d (μa).	$E_{\frac{1}{2}}$ (volts).	Viscosity (η).	$i_d\,\eta^{\frac{1}{2}}$.
		KCl.				KNO_3.		
M/10	2.150	0.612	1.004	2.154	..	..	0.998	..
M/2	2.175	0.632	1.017	2.194	1.500	0.595	0.980	1.485
M	2.200	0.647	1.019	2.220	1.500	0.595	0.974	1.480
2*M*	2.225	0.660	1.073	2.305	1.500	0.595	0.958	1.468
		NH_4Cl.				HCl.		
M/10	..	..	1.000	..	3.000	0.640	1.009	3.013
M/2	1.750	0.642	0.986	1.740	3.000	0.675	1.063	3.092
M	1.900	0.670	0.985	1.886	3.000	0.720	1.112	3.163
2*M*	1.750	0.687	0.980	1.732	3.000	0.757	1.214	3.321

TABLE II

Zn^{2+} *as the reducing ion.*

Supporting electrolyte conc.	i_d (μa).	$E_{\frac{1}{2}}$ (volts).	Viscosity (η).	$i_d\eta^{\frac{1}{2}}$.	i_d (μa).	$E_{\frac{1}{2}}$ (volts).	Viscosity (η).	i_d (η)$^{\frac{1}{2}}$.
		KCl				KNO_3		
M/10	1.000	1.100	1.002	1.000	1.450	1.080	0.993	1.445
M/2	1.050	1.065	0.984	1.041	1.475	1.110	0.984	1.464
M	1.650	1.0425	0.981	1.634	1.500	1.110	0.966	1.474
2*M*	1.950	1.040	0.972	1.923	1.525	1.062	0.962	1.495
		NH_4Cl.						
M/10	1.700	1.120	0.993	1.694				
M/2	1.700	1 170	0.999	1.698				
M	1.700	1.115	0.993	1.694				
2*M*	1.650	1.130	0.994	1.641				

It will be evident from the columns of viscosity that in presence of Cd^{2+} ions (of the concentration of the order of 10^{-4} *M*) viscosities of KCl and HCl solutions slightly increase with increasing concentration, whereas those with KNO_3 and NH_4Cl exhibit a slight diminution. In the case of Zn^{2+} ion (present in the same concentration) the salts, KCl and KNO_3, uniformly show slight diminution of relative viscosity with increasing concentrations of the supporting electrolytes. Such a behaviour is not quite unexpected, as studied by Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 2950) as well as by Joy and Wolfenden (*Proc. Roy. Soc.*, 1932, **134A,** 424) who related viscosity with concentration from the point of view of the Debye-Hückel theory and obtained a complicated relationship (vide Gurney, "Ionic Processes in Solution", McGraw Hill Book Co. Inc., 1953, p. 160).

The diffusion current i_d increases with increasing KCl concentration in the case of Cd^{2+} and Zn^{2+} ions, whereas in both the cases it remains constant in the cases of KNO_3 and NH_4Cl. With HCl, however, the case of Cd^{2+} could only be studied; i_d was found to remain constant in spite of the change in viscosity.

The half-wave potential shows a slight increase with concentration of the supporting electrolytes KCl, NH_4Cl, and HCl in the case of Cd^{2+}. With KNO_3 and Cd^{2+} ion, $E_{\frac{1}{2}}$ remains almost at a constant value. In the case of Zn^{2+} ion, all the three electrolytes, KCl, KNO_3, and NH_4Cl, showed almost constant $E_{\frac{1}{2}}$ at all concentrations.

Coming back again to the case of Cd^{2+} and KCl, we find that with increasing concentration of KCl both i_d and η increase. $i_d\eta^{\frac{1}{2}}$ also shows a regular increase. This appears to be

peculiar beause i_d should diminish with viscosity. If the former were dependent on viscosity alone, as reported earlier (*loc cit.*), $i_d\eta^{\frac{1}{2}}$ should remain constant. But a systematic increase of the product definitely shows that there is some other factors appearing which may be responsible for the increase in i_d beyond proportions. What this other factor may be, is difficult to anticipate off hand. From the literature (Kolthoff and Lingane, "Polarography", Vol. I, 2nd ed., 1952, p. 96) we find that in presence of Cl^- ions both Cd^{2+} and Zn^{2+} have tendencies to form complexes $CdCl^+$ and $ZnCl^+$ which being monovalent will be expected to have a high diffusion coefficient according to the equation in which the valency Z appears in the denominator:

$$D^\circ = 2.67 \times 10^{-7} \frac{\lambda^\circ}{Z} \text{ (cm}^2 \text{ sec}^{-1} \text{ at } 25^\circ\text{)}$$

The case of Zn^{2+} and KCl appears to have a more marked but similar effect. The same cause may also be responsible in this case too. The case of Cd^{2+} and HCl is similar probably due to the same reason.

Using KNO_3 as the supporting electrolyte, there is hardly any change in the product $i_d\eta^{\frac{1}{2}}$ with Cd^{2+} ion. There appears to be a slight decrease at a concentration of $2M$-KNO_3 which may be due to the effect of viscosity being quite less at this high concentration. In the case of Zn^{2+} and KNO_3, the product, $i_d\eta^{\frac{1}{2}}$, shows slight increase with increasing concentration, similar to Zn^{2+} and KCl, but the effect is less marked in this case. What this is due to, is not very clear. It may be that Zn^{2+} has a tendency to form a complex with NO_3^- ion also even at such an ionic strength as has been suggested in the case of Cd^{2+} by Meites ("Polarographic Techniques", Interscience Publishers, 1955, p. 124).

In presence of NH_4Cl and Cd^{2+}, the values of i_d are slightly less than those with KCl but greater than those in KNO_3 and they show little variation with concentration. The half-wave potentials of Cd^{2+} in KCl and NH_4Cl are almost of the same order, but concentrations of NH_4Cl have very little influence on $E_{\frac{1}{2}}$. $E_{\frac{1}{2}}$ values in presence of KNO_3 are decidedly the lowest, but those with HCl show higher values. Viscosity (η) appears to show no change with concentration of NH_4Cl and therefore the product $i_d\eta^{\frac{1}{2}}$ remains almost constant as expected. With Zn^{2+} and NH_4Cl, i_d shows practically no change unlike the case of KCl or KNO_3. $E_{\frac{1}{2}}$ also remains practically constant in this case and product $i_d\eta^{\frac{1}{2}}$ shows the constant expected values.

It is to be noted in this connection that with Cd^{2+} in presence of KCl and HCl, there a possibility of complex formation of Cd^{2+} and Cl^- ions and so the peculiar behaviour, as mentioned above, appears with NH_4Cl also. The case shows, however, no abnormality but always yields a normal behaviour. Whether this is due to the absence of the complex formation or due to any effect of the NH_4 ion cannot, however, be ascertained without further investigation. Kolthoff and Lingane (*loc cit.*, p. 97) refers to the formation of ammonia complex with both Cd^{2+} and Zn^{2+} in an ammoniacal medium of NH_4Cl. The present case, however, differs from that mentioned by Kolthoff and Lingane. Whether complex formation of Cd^{2+} and Zn^{2+} ions occurs simultaneously with NH_4^+ and Cl^- ions and how far such a possibility can explain this fact are not yet understood.

Thanks of the authors are due to the government of India for the award of a research fellowship to one of them (A. C.) for which it was possible to undertake this investigation.

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Received June 6, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Dihydroisocoumarins. Part II. Synthesis of 3,4-Dihydro-6,7-dimethoxyisocoumarin

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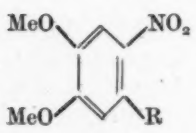
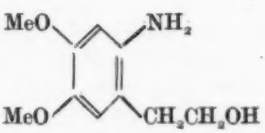
The synthesis of 3,4-dihydro-6,7-dimethoxyisocoumarin (III) has been effected.

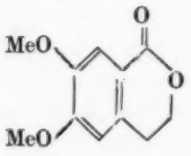
In Part I of this series, the synthesis of 3,4-dihydro-7,8-dimethoxyisocoumarin has been reported (Banerjee and Chaudhury, *J. Org. Chem.*, 1961, **26**, in press). The present communication deals with the synthesis of the isomeric 3,4-dihydro-6,7-dimethoxyisocoumarin (III). 4,5-Dimethoxy-2-aminophenethyl alcohol (II), the key compound for the synthesis of the dihydroisocoumarin (III), was prepared by two routes. Nitration of methyl homoveratrate ("Org. Syn.", 1943, Coll. Vol., II, p. 333) at 0° yielded almost exclusively methyl-6-nitrohomoveratrate (I: R=CH_2COOMe), the orientation of which was established by comparison with an authentic specimen prepared from 6-nitrohomoveratric acid (I:R=CH_2COOH) (Hahn and Schulz, *Ber.*, 1939, **72**, 1312) with an excess of ethereal diazomethane. In the synthesis of 3,4-dihydro-7,8-dimethoxyisocoumarin (*loc. cit.*), it has been shown that $LiAlH_4$ reduction of methyl 2-nitrohomoveratrate afforded a mixture of 2,3,2′,3′-tetramethoxy-6,6′-dihydroxyethylazobenzene and 2-nitrohomoveratryl alcohol, which as such or separately, when reduced with sodium dithionite, gave 3,4-dimethoxy-2-aminophenethyl alcohol. Accordingly, adopting the same procedure methyl 6-nitrohomoveratrate (I : R=CH_2COOMe) was reduced successively with $LiAlH_4$ and sodium dithionite to yield 4,5-dimethoxy-2-aminophenethyl alcohol (II), isolated as its hydrochloride.



(I)



(II)



(III)

In an alternative procedure, homoveratryl alcohol (Howell and Taylor, *J. Chem. Soc.*, 1956, 4252) on nitration at 0° gave 6-nitrohomoveratryl alcohol (I:R=CH_2CH_2OH) which was reduced with sodium dithionite to 4,5-dimethoxy-2-aminophenethyl alcohol (II); this transformation incidentally proved the orientation of the nitro-alcohol (I: R=CH_2CH_2OH).

Finally, diazotisation of (II), its conversion into the nitrile (which was not purified), and subsequent alkaline hydrolysis, followed by acidification, gave 3,4-dihydro-6,7-dimethoxyisocoumarin (III).

*EXPERIMENTAL

Methyl 6-Nitrohomoveratrate (I: R=CH_2COOMe).—Methyl homoveratrate (5 g.) was added portionwise to HNO_3 (25 c.c., *d* 1.42) with constant stirring; the temperature during addition was not allowed to rise above 0°. The reaction mixture was left at 10° for an hour and then poured into ice-water (250 c.c.). The precipitate was filtered after an hour, washed thoroughly with water, and recrystallised from methanol as yellow needles (4.5 g.), m.p. 116-17°. (Found: C, 51.5; H, 5.2. $C_{11}H_{13}O_6N$ requires C, 51.76; H, 5.09%).

6-Nitrohomoveratryl Alcohol (I:R=CH_2CH_2OH).—Homoveratryl alcohol (1.6 g.) was added in portions to HNO_3 (9 c.c., *d* 1.42) with constant stirring, the temperature being maintained at 0°. The reaction mixture after being kept at 5° for half an hour was poured into ice-water (200 c.c.) when a yellow precipitate was obtained. It was filtered, washed thoroughly with ice-cold water, and dried in a desiccator. Repeated crystallisations from ethyl acetate-petroleum ether (b.p. 60-80°) furnished irregular prisms, m.p. 107°, yield 0.7g. (Found: C, 52.2; H, 5.6. $C_{10}H_{13}O_5N$ requires C, 52.8; H, 5.7%).

4,5-Dimethoxy-2-aminophenethyl Alcohol (II): *Method* (*a*).—A solution of methyl 6-nitrohomoveratrate (I: R=CH_2COOMe) (1.5 g.) in dry THF (30 c.c.) was added dropwise to a stirred suspension of $LiAlH_4$ (0.6 g.) in dry THF (25 c.c.), cooled to -15°, and left overnight at room temperature. Unchanged $LiAlH_4$ and the complex were decomposed by careful portionwise addition of ice-water (10 c.c.) followed by 2*N*-H_2SO_4 (40 c.c.). It was extracted with ether (3×50 c.c.). The combined ether extract was dried (K_2CO_3) and evaporated to a dark red solid which was dissolved in methanol (25 c.c.) and water (10 c.c.). Sodium dithionite (2 g.) was added in portions when the dark red colour was immediately discharged to a pale yellow solution and it was refluxed on a water bath for half an hour. After distilling most of the methanol, the solution was repeatedly extracted with chloroform (3×40 c.c.), the yellow chloroform solution extracted with 50% HCl (2×25 c.c.), and separated. The acid solution was cooled, mixed with chloroform (25 c.c.), basified carefully with ammonia (*d* 0.88), and vigorously shaken. The chloroform layer was separated and the aqueous layer further extracted with chloroform (2×25 c.c.). The combined chloroform extract was dried (Na_2SO_4) and the solvent distilled to yield the amino-alcohol (II) as a red oil which soon solidified to yellow needles, m.p. 84-86°. As it rapidly underwent oxidation in air, it was immediately taken up in dry ether (25 c.c.), chilled to -15°, and dry hydrogen chloride bubbled through when the *amine hydrochloride* (0.375 g.) separated as dark needles. After recrystallisation from methanol-ether it was further purified by sublimation *in vacuo* (bath temp. 160°/0.1 mm) as white needles, m.p. 197-98°. (Found: C, 51.4; H, 6.2. $C_{10}H_{16}O_3NCl$ requires C, 51.3; H, 6.4%).

Method (*b*).—6-Nitrohomoveratryl alcohol (I : R=CH_2CH_2OH) (1 g.) in methanol (25 c.c.) and water (10 c.c.) was refluxed with sodium dithionite (3.5 g.) for half hour. During this period water (10 c.c.) was added in instalments to dissolve the sodium dithionite, when a clear solution was obtained. It was cooled, methanol distilled, and the aqueous solution extracted with chloroform (3×15 c.c.). The chloroform solution was treated as in method (*a*) to isolate the amino-alcohol (II) as its *hydrochloride* (0.6 g.), m.p. 197-98°, undepressed on admixture with the specimen obtained by method (*a*).

* All m.p's are uncorrected. Microanalyses by Dr. Gore, Dept. of Chemical Technology, University of Bombay.

3,4-*Dihydro*-6,7-*dimethoxyisocoumarin* (III).—The hydrochloride of (II) (0.380 g.) in HCl (0.38 c.c., *d*1.16) and water (9 c.c.) was diazotised with sodium nitrite (0.12 g.) in water (1 c.c.) at 0-2°. After neutralisation with sodium carbonate, the diazonium solution was added to a solution of KCN (0.380 g.), nickel chloride (0.300 g.) and anhydrous sodium carbonate (0.1g.) in water (10 c.c.) at 15° with stirring. The mixture was allowed to stand for 2 hours at 15° and then heated to 75° for 45 minutes. The solution was cooled, extracted with ether (4×20 c.c.), the combined ether extract was dried (Na_2SO_4), and the ether distilled to give a red gum. The gum was refluxed with aqueous KOH (20 c.c., 10 %) for 4 hours, cooled, and acidified with HCl (conc.) (Congo red). The solution was filtered and extracted with chloroform (3×25 c.c.), the extract dried (Na_2SO_4), and the solvent evaporated to give a gum which solidified on standing overnight to yellow needles. It was sublimed *in vacuo* (bath temp.120-25°/0.1 mm) to yield a white solid, m.p. 134-36°. Recrystallisation from ethyl acetate-petroleum ether (b.p. 60-80°) afforded 3,4-*dihydro*-6,7-*dimethoxyisocoumarin* as colorless needles (0.21 g.), m.p. 140-41°. (Found: C, 63.0; H, 5.5. $C_{11}H_{12}O_4$ requires C, 63.4; H, 5.7%). I. R. in $CHCl_3$: 5.88μ (conjugated δ-lactone).

The authors wish to thank Dr. Tapan K. Mukherjee, Retina Foundation, Boston 14, Mass., U.S.A., for the I. R. data and the U. G. C. for the award of a research scholarship to one of them (J. N. S.).

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Received July 10, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

Vanadium. Part I. Quinaldinic Acid Complexes

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Quinaldinic acid (QH) produces with vanadyl salt (1) a cream-coloured compound, characterised as $[VOQ_2]$ H_2O and (2) an olive-green complex $[VO(H_2O)Q_2]$. Both change on heating to cream-coloured $[VOQ_2]$ and finally decompose to V_2O_5. A whole series of bluish green complexes of the type $[VO(X)Q_2)]$ (where X= pyridine, aniline, etc.) has been prepared by the action of aromatic amine or heterocyclic base on either $[VOQ_2]$ H_2O or on $[VO(H_2O)Q_2]$. These, too, change on heating to $[VOQ_2]$. All these products are paramagnetic (μ = 1.6 to 1.9 B.M.) and are extremely stable towards air.

Quinquevalent vanadium reacts with this ligand to give pale cream-coloured, diamagnetic $[VO(OH)Q_2]$-$2H_2O$. Compounds of the type $[VO_2Q\ (X)]$ (where X=pyridine or α-picoline) have been prepared by the action of heterocyclic bases on $[VO(OH)Q_2]$ $2H_2O$.

Complex compounds of quadrivalent vanadium with oxalic, malonic, and salicylic acids and with catechol are already known (Sidgwick, "Chemical Elements and their Compounds", Vol. I, Oxford University Press, 1951, p. 822). The vanadyl acetylacetone complex has been studied by Morgan and Moss (*J. Chem. Soc.*, 1913, **103**, 78), by Rosenheim and Mong (*Z. anorg. Chem.*, 1925, **148**, 25), and also by Jones (*J. Amer. Chem. Soc.*, 1954, **76**, 5995). Drew and Dunton (*J. Chem. Soc.*, 1940, 1064) have described some fairly stable, six-covalent complexes of hydroxyazo and amino-azo dyes. Pfeiffer *et al.* (*J. prakt. Chem.*, 1937, **149**, 217) and also Mukherjee and Rây (this *Journal*, 1955, **32**, 508) have reported some complexes with Schiff's bases. Bradley *et al.* (*J. Chem. Soc.*, 1858, 4647) have studied some six-co-ordinated alkoxide alcoholates which exist only at a low temperature. Some vanadyl biguanidines have recently been described by Banerjee and Rây (Proceedings of the Symposium on the Chemistry of Co-ordination Complexes, Agra, National Academy of Sciences, Part III, 1959, p. 198). Trujilo *et al.* (*Chem. Abs.*, 1956, **50**, 16528; 1957, **51**, 11907; 1958, **52**, 1966; 1959, **53**, 21343; 1960, **54**, 2076) have studied in solution the system vanadyl malonate, phosphotungstate, acetylacetonate, *o*-phenanthrolinate, etc.

Quinquevalent vanadium complexes are not many. The important ones are those with 8-hydroxyquinoline, studied in great details (Welcher, "Organic Analytical Reagents", Vol. I, p. 297; Bielig *et al.*, *Annalen*, 1953, **584**, 96; Blair *et al.*, *J. Inorg. Nucl. Chem.*, 1958, **5**, 316) and with salicylaldoxime (Bielig and Mollinger, *Annalen*, 1957, **605**, 117).

In this laboratory, a variety of organic ligands, namely, quinaldinic acid and its derivatives, hydroxamic acids,* hydroxyphenyltriazenes, benziminazoles, benzotriazoles, oximes, etc., are now being investigated as chelating ligands towards various oxidation states of vanadium**. In this, the first paper of the series, we report the complexes of quadri-

*These have been extensively studied by Dutta and also by other workers as sensitive colorimetric reagents for vanadium (Dutta, this *Journal*, 1958, **35**, 243; 1959, **36**, 285, 229; Dasgupta and Singh, *J. Sci. Ind. Res.*, 1952, **11B**, 268; Bhaduri and Rây, *Z. anal. Chem*, 1957, **154**, 103; Wise and Brandt, *Anal. Chem.*, 1955, **27**, 1392).

** A priliminary report on the vanadium complexes of hydroxyphenyltriazenes has already appeared (Dutta and Lahiry, *Chem. & Ind.*, 1961, 78).

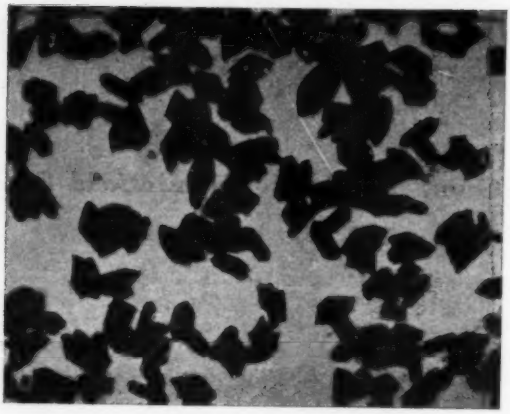


FIG. 1. Olive-green aquo-oxo-bis-quinaldinato-vanadium (IV).

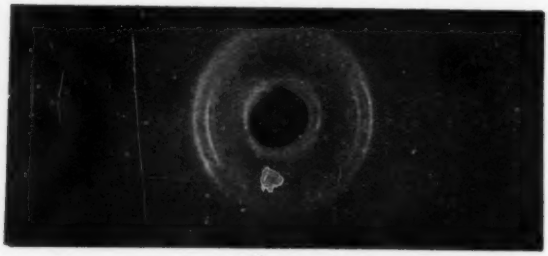


FIG. 2. Oxo-bis-quinaldinato-vanadium (IV) monohydrate (cream).
θ°=4.0; 5.5; 10.5; 11.5; 13.25; 18.00; 19.5; 21.5; 23.75.
d(Å)=11.03; 8.04; 4.22; 3.86; 3.36; 2.79; 2.31; 2.10; 1.91.

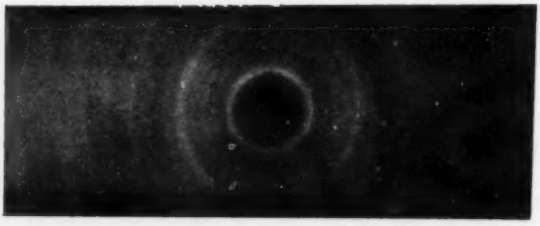
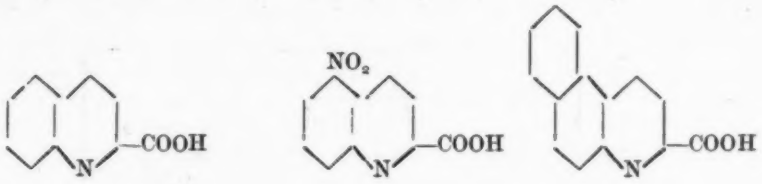


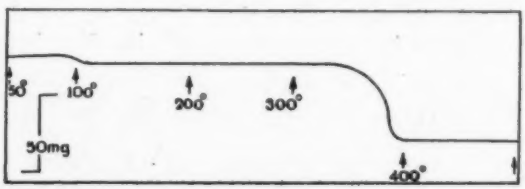
FIG. 3. Aquo-oxo-bis-quinaldinato-vanadium (IV) (olive-green).
θ°=6.5; 8.5; 10.5; 12.0; 13.5; 14.0; 16.5; 18.75; 21.25.
d(Å)=6.8; 5.21; 4.23; 3.70; 3.30; 3.18; 2.71; 2.39; 2.12.

and of quinquevalent vanadium with quinaldinic acid (quinoline-2-carboxylic acid) and its 5-nitro and 5,6-benzo derivatives, describing first the quadrivalent vanadium compounds.



Quadrivalent Vanadium Complexes

On the addition of vanadyl sulphate to an aqueous solution of quinaldinic acid (QH), a cream-coloured, voluminous precipitate is obtained at *p*H about 3. The precipitation is quantitative within the *p*H range 4 to 6, but appears to be of little value for analytical purpose as the reaction can be substantially suppressed by masking agents, e.g., tartaric acid. This precipitate, after being washed with water and drying over $CaCl_2$, corresponds to the composition, $VOQ_2 . H_2O$ (I). On the other hand, when aqueous vanadyl sulphate is added to a methanolic solution of quinaldinic acid and the mixture is allowed to stand overnight, a highly crystalline, glistening, deep olive-green compound (vide Microphotograph, Fig. 1) is obtained, which again, corresponds to the same composition, $VOQ_2.H_2O$ (II). That these two compounds are different and that the difference in colour is not due to a difference in crystal size have been verified through a study of the two X-ray powder patterns. Comparison of the two diffraction patterns show that the structures of the two substances are different. From the data it is observed that at small angles the cream-coloured sample has two very strong lines corresponding to *d* values of 11.03 Å and 8.04 Å and further out they have two more very strong lines of '*d*' values 3.86 Å and 3.36 Å. On the other hand, the strongest line of the olive-green sample has the '*d*' value 6.80 Å. Further out it shows a pair of medium strong lines of '*d*' values 3.30 Å and 3.18 Å. Furthermore, compound (I) can be dehydrated by heating to the penta-co-ordinated $[VOQ_2]$. Compound (I) also loses partially its water content in vacuum. Compound (II), however, does not lose any water in vacuo, but does so on heating and changes from olive-green to the cream-coloured $[VOQ_2]$. In order to have a better insight into the nature of these two varieties, we have obtained the pyrolysis curves of these. It would appear from Fig. 4 that the cream-coloured $[VOQ_2]$-



Temp.

Fig. 4. Pyrolysis of cream-coloured oxo-bis-quinaldinato-vanadium (IV) monohydrate.

H_2O loses water at 90-100° and then the anhydrous $[VOQ_2]$ decomposes at 380-400° to V_2O_5, which remains stable thereafter. As against this, the pyrolysis curve (Fig. 5) of the olive-

green variety (II) shows that the water is lost at 155-65° and thereafter the nature of the pyrolysis curve is identical with that of (I). This evidently shows that the water molecule in the olive-green variety is held much more strongly than in the cream-coloured one. We may therefore conclude that the H_2O molecule in (II) is present inside the co-

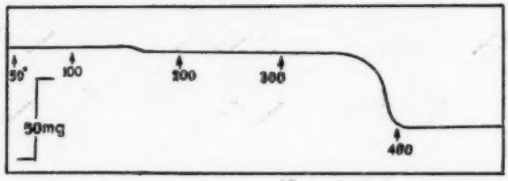
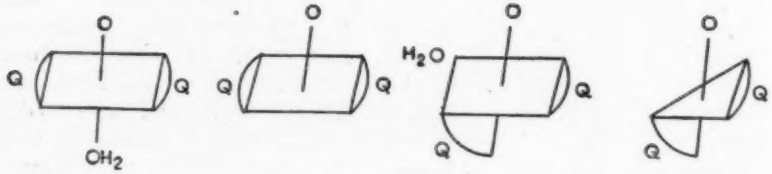
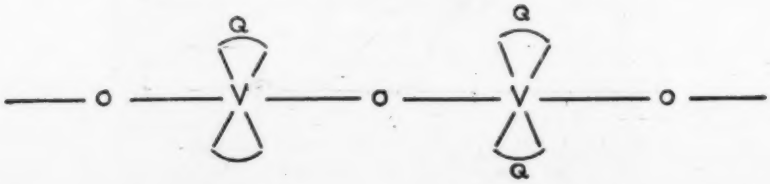


Fig. 5. Pyrolysis curve of olive-green coloured aquo-oxo-bis-quinaldinato vanadium (IV).

ordination zone, giving the complex an octahedral structure, whereas the H_2O in (I) is held in the crystal lattice, rather than in the inner sphere. Thus the cream-coloured $[VOQ_2]\cdot H_2O$ or the anhydrous VOQ_2 is, in reality, a penta-co-ordinated complex, unless one assumes the rather improbable feature of one 'O' taking two co-ordination positions. The pyrolysis curves reveal something more. The curves of compounds (I) and of (II) are identical after the loss of the water molecule. This means in both cases the remaining $[VOQ_2]$ has the same structure. A compound, such as is $[VOQ_2]$, can have two possible structures, a square pyramid or a trigonal bipyramid.



If in the olive-green compound the 'O' and 'H_2O' are *trans* to one another, then the anhydrous compound will have a square pyramid structure. On the contrary, if 'OH_2' is *cis* to 'O', then the loss of 'OH_2' would result in a trigonal bipyramid structure. Since the *trans* structure is generally more stable than the *cis*, we would prefer to conclude that the olive-green compound has *trans* structure and that the anhydrous compound has



therefore a square pyramid configuration. One, however, cannot rule out the possibility of a polymeric structure for $[VOQ_2]$, but the very poor solubility of the substance in all

common organic solvents, such as ethanol, acetone, benzene, chloroform, *o*-dichlorobenzene, etc., has made impossible the determination of its molecular size.*

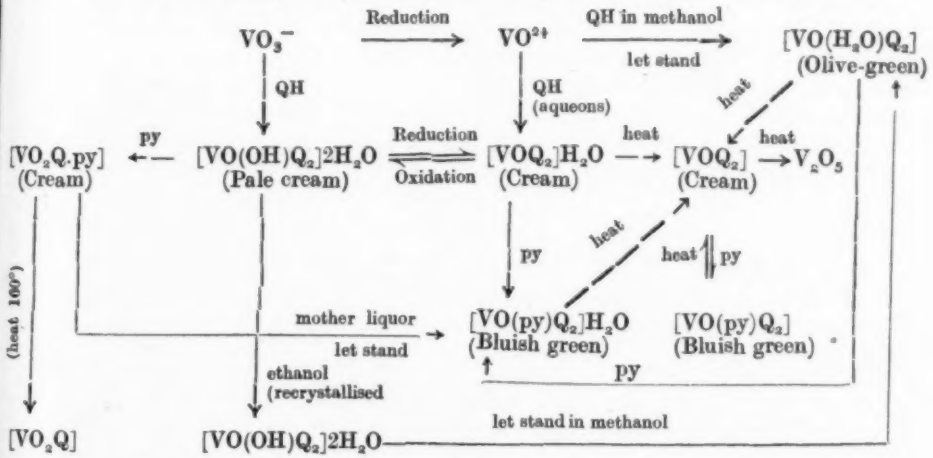
The infrared spectra of these complexes have also been studied with the same purpose. According to Fujita *et al.* (*J. Amer. Chem. Soc.*, 1956, **78**, 3963) the band due to co-ordinated water appears at 800 cm^{-1} to 1000 cm^{-1}. But Jones (*loc. cit.*) has considered a band at 3200 cm^{-1} to 3600 cm^{-1} as diagnostic of the co-ordinated water inside the sphere of vanadyl acetylacetonates. On comparing the spectra of (I) with that of (II) (Fig. 7) one hardly finds any perceptible difference (excepting a reversal of intensity of the two bands at 910 cm^{-1} and 970 cm^{-1}. We cannot be sure of an aqua band in either of these complexes, as both the regions 800-1000 cm^{-1} and 3200-3600 cm^{-1} have strong absorption bands due to other groups, namely, 'VO' and 'CH' (Bellamy, "Infrared Spectra of Complex Molecules"). The sharp peak at 970 cm^{-1} is due certainly to the vanadyl band. Bielig *et al.* (*loc. cit.*) have observed this band in oxo-hydroxo-bis-oxinato-vanadium (V) at 950 cm^{-1}, Blair *et. al.* (*loc. cit.*) at 952 cm^{-1}, and Nyholm *et al.* (*J. Chem. Soc.*, 1959, 3552) at 980-995 cm^{-1} in general for metal-oxygen bonds. We find, that the pyrolysis curves, rather than the infrared spectra, have been of better value in appreciating a difference between these two differently coloured varieties of vanadyl quinaldinate.

The action of a series of ammines and heterocyclic bases on the two modifications, (I) and (II), has been investigated with a view to elucidating the preference of a sexa-co-ordination to a penta-co-ordination as also to have an idea of the stability of these ammine-containing complexes. Thus compound (I) while still moist, on being heated with pyridine,

CHART I

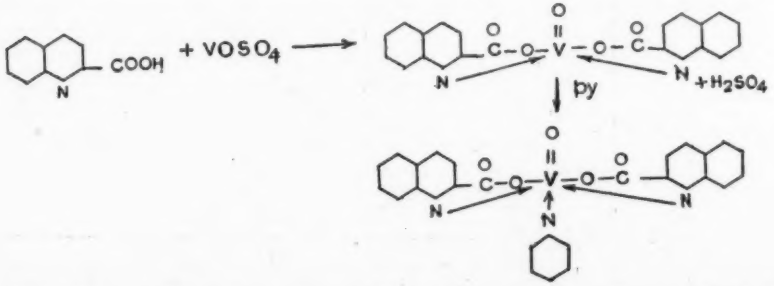
[QH = quinaldinic acid; = py pyridine]

General scheme of the reactions of V^{IV} *and of* V^{V} *with quinaldinic acid.*



*In this connection mention may be made here of an interesting, recent structural investigation of oxo-bis-acetylacetonato-vanadium (IV) which reveals that the five oxygen atoms are at the corners of an approximately square pyramid, but that the vanadium is near the centre of gravity of this pyramid, rather than at the centre of its base (Dodge, Templeton and Zalkin, Chemistry Division Annual Report, 1960 p. 203; published February, 1961, Radiation Laboratory, Berkeley, California; *J. Chem. Phys.*, 1961, **35**, 1,55).

readily dissolves to produce a greenish brown solution, which soon deposits fine bluish green crystals of the composition $[VO(py)Q_2]H_2O$. This compound loses its pyridine and water on heating; first water is lost, then the pyridine, and finally the colour changes to cream resulting in the formation of $[VOQ_2]$. The olive-green variety (II) on treatment with pyridine produced identical bluish green crystals of $[VO(py)Q_2]H_2O$, having the same properties. The pyridine complex is quite stable at ordinary temperature. The action of pyridine on the anhydrous $[VOQ_2]$ resulted in the separation of bluish green crystals of composition $[VO(py)Q_2]$. This compound furnishes an evidence to the effect that the pyridine molecule is inside the co-ordination sphere, as otherwise, with pyridine of crystallisation there is not much ground for the compound changing its colour from cream to bluish green. We have also obtained the infrared spectra of both $[VO(py)Q_2]H_2O$ and also of $[VO(py)Q_2]$ (Fig. 8.). Besides showing all the characteristic bands of the cream-coloured $[VOQ_2]H_2O$ and of the olive-green $[VO(H_2O)Q_2]$, these bluish green varieties present a new, sharp, and strong band at 700-710 cm^{-1}, which is certainly related to the presence of a heterocyclic pyridine in the molecule (Bellamy, *loc. cit.*). But, again, the spectra do not help to clarify the position of the aqua molecule. The sixth co-ordination position in the octahedron of vanadyl quinaldinate has also been variously filled up with amines, such as, α-picoline, aniline, methylanthranilate, diphenylamine, and also by dimethylformamide. The α-picoline and the methylanthranilate complexes could not be obtained by heating $[VOQ_2]H_2O$ with the amine, instead the $[VOQ_2]H_2O$ was left in contact with the amine. The dimethylformamide compound is the darkest bluish green in the whole series. β-Naphthylamine also produced a light bluish green product, which unfortunately did not provide satsifactory analytical results. Ammonia or aliphatic amines dissolved $[VOQ_2]H_2O$ producing a brown solution, indicating probably oxidation to the pentavalent state. The aliphatic amines are much stronger bases compared to aromatic amines and pyridine and hence have a strong alkaline action resulting in oxidation. Indeed, addition of $VOSO_4$ to an alkaline QH solution produces a light brown solution. Ligands, such as, quinoline, isoquinoline, and quinaldine, failed to produce any bluish green product. This, no doubt, is related to the bigger size of the ligand molecule, which is difficult to fit into the octahedron. We have also investigated the action of dioxan, tetrahydrofuran* (typical of co-ordination through 'O'), and also of thiophen (co-ordination through S). In all these cases light bluish green to light green products were obtained. We may therefore conclude that the tendency of quadrivalent vanadium to assume an octahedral structure is quite prominent.



Like the amine complexes, these compounds also lose on heating the co-ordinated dioxan,

*This is well known to have the ability of stabilising lower valent states of metals in complexes *e.g.*, in Li $[Ti(bipy)_3]$. 3.5-C_4H_8O (Herzog and Taube, *Angew Chem.*, 1958, **70**, 469).

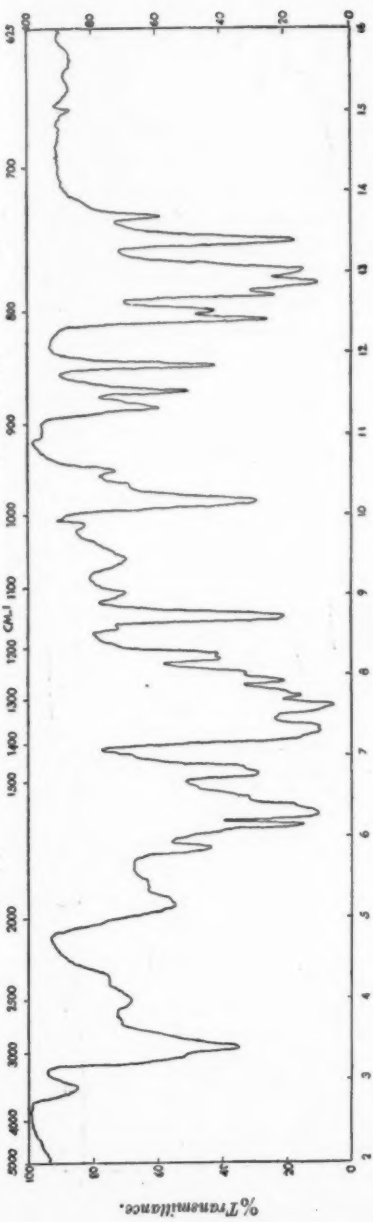


FIG. 6. I. R. spectra of quinaldinic acid.

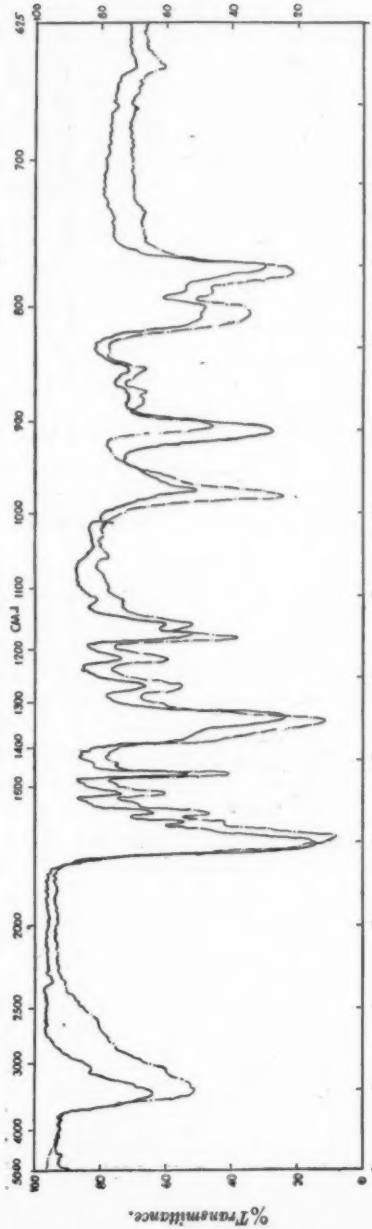


FIG. 7. I. R. spectra of oxo-bis-quinaldinato-vanadium (IV) monohydrate (—) and of aquo-bis-quinaldinato-vanadium (IV) (—·—·—)

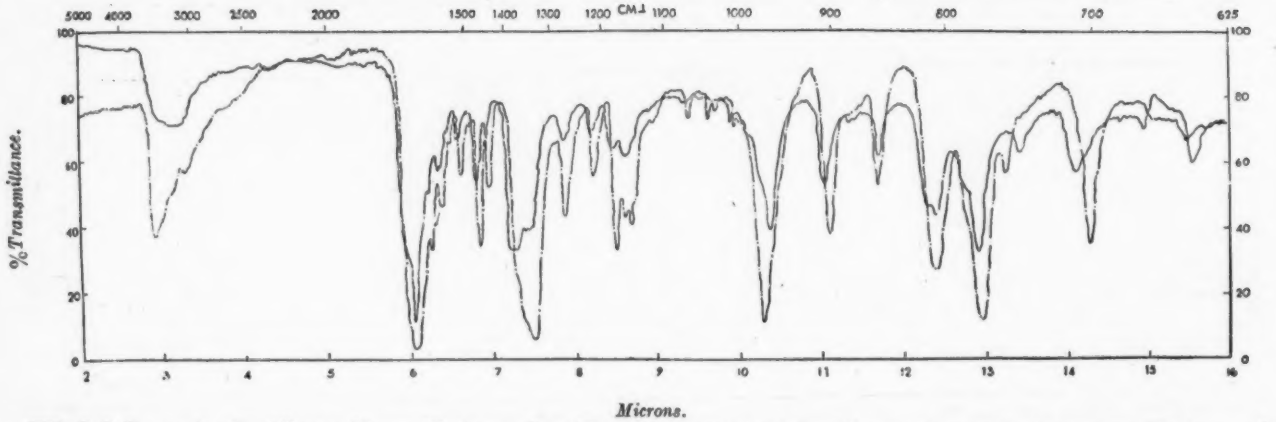


FIG. 8. I. R. spectra of pyridine-oxo-bis-qunaldinato-vanadium (IV) monohydrate (—) and of pyridine-oxo-bis-quinaldinato-vanadium (IV) (—.—.—)

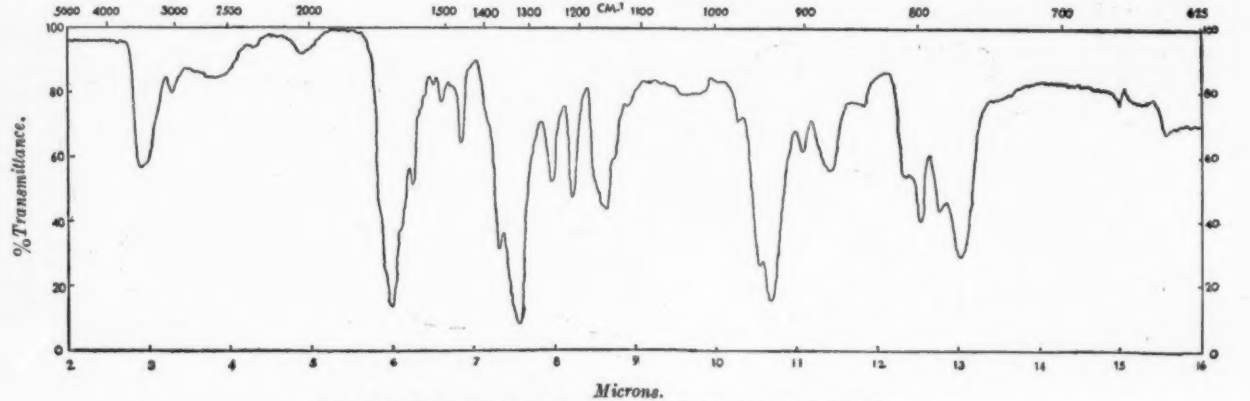


FIG. 9. I. R. spectra of oxo-hydroxo-bis-quinaldinato-vanadium (IV).

tetrahydrofuran, and thiophen, though somewhat more readily. By the action of KCN on $[VOQ_2]$ we have obtained a greenish black powder which is now under investigation. We intend to study thoroughly the action of KCN on a variety of stable vanadium (IV) complexes.

The quadrivalency of vanadium in the above described complexes has been established through the determination of the magnetic moments. Vanadium in the 4^+ oxidation state is a d^1 ion, so that a magnetic moment of the order of 1.73 B.M. is expected. The compounds, so far described, show moment values lying between 1.6 and 1.9 B.M. An octahedral d^2sp^3 or a square pyramid d^2sp^2 hybrid co-ordination is indicated. Attempts were also made to determine the oxidation state by titrimetry against standard permanganate. The results were not to our entire satisfaction, the end point being rather fleeting. It is not unlikely that the ligand is also affected by the permanganate.

Two other derivatives of quinaldinic acid, namely, 5-nitroquinaldinic acid and 5,6-benzoquinaldinic acid, were found to give only the paramagnetic pale apple-green to cream-coloured variety of quadrivalent vanadium complexes. The compounds lose one molecule of water at 140-50°, indicating that the complexes are octahedral with the H_2O inside the co-ordination sphere. Surprisingly enough, they failed to give any bluish green product with aromatic amines or the heterocyclic bases, the original compounds being recovered unchanged.

Quinquevalent Vanadium Complexes

A curdy white precipitate appears on the addition of quinaldinic acid to aqueous ammonium vanadate. This on purification from hot ethanol gives the composition $[VO(OH)Q_2]\ 2H_2O$. The compound is diamagnetic. That the alternative formula $H[VO_2Q_2]\ 2H_2O$ does not reveal the exact state, is proved through its poor conductance (2.24 mhos) in methanol. On allowing a methanolic solution (0.001*M*) of the product to stand for two weeks, there appeared some glistening olive-green crystals. The compound was then prepared by repeated refluxing of $[VO(OH)Q_2]\ 2H_2O$ with a large volume of methanol. This was found to be identical with the compound (II), described under quadrivalent vanadium. Thus on standing or on refluxing in methanol $[VO(OH)Q_2]$ is reduced to $[VO(H_2O)Q_2]$. On heating $[VO(OH)Q_2]$ with pyridine, two products were obtained: (*a*) the first is colorless $[VO_2Q.py]$, one QH being knocked off; (*b*) the mother liquor on standing furnishing low yields of $[VO(py)Q_2]H_2O$. The compound $[VO_2Q.py]$ is diamagnetic, indicative of the quinquevalency of vanadium. The pyridine in the compound is held very strongly and is not lost before 160°. The product after the loss of pyridine gave analyses for $[VO_2Q]$, which should be regarded as a four co-ordinated complex of vanadium (V). The second product has a bluish green colour, identical with the one obtained from $[VO_2(H_2O)Q_2]$ by the action of pyridine. A similar reaction also occurred with α-picoline. The compound, $[VO_2Q.py]$ presumably has a square pyramid structure. Corresponding products with aniline and dimethylformamide did not give very satisfactory analyses.

The infrared spectral characteristics of the compound $[VO(OH)Q_2]\ 2H_2O$ were also studied. Besides showing the same absorption characteristics as shown by $[VO(H_2O)Q_2]$ and $[VOQ_2]H_2O$, this compound reveals one extra band, sharp but of low intensity at about 3100 cm^{-1}. Bielig *et al.* (*loc. cit*) attribute a weak band at about 3400 cm^{-1}

to be due to OH in the compound oxo-hydroxo-bis-oxinato-vanadium (V). At the region 3400 cm^{-1} all our samples, however, show prominent absorption bands. As the band at 3100 cm^{-1} does not appear in our other compounds, this may be assigned to the OH in the compound, oxo-hydroxo-bis-quinaldinato-vanadium (V). In fact, there are evidences to show that the OH band appears near 3100 cm^{-1} (Cross, "Practical Infrared Spectroscopy", Butterworths Publication, 1960).**

TABLE I

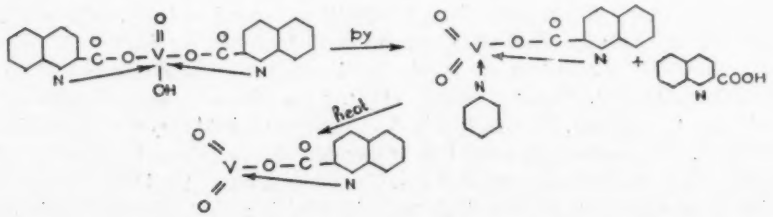
Magnetic measurements.

Temp.=35°.

Compounds.	Dia. corr.$\times 10^6$.	χ_M (corr.)$\times 10^6$.	μ_{eff} (B.M.)*.
$[VOQ_2]H_2O$	208.4	1236	1.75
$[VO(H_2O)Q_2]$	208.4	1264	1.77
$[VO(C_5H_5N)Q_2]H_2O$	259.0	1397	1.86
$[VO(CH_3.C_5H_4N)Q_2]$	257.9	1320	1.81
$[VO(C_6H_5.NH_2)Q_2]$	258.8	1312	1.805
$[VO(C_6H_4(NH_2)(COOCH_3))Q_2]$	284.9	1550	1.96
$[VO(HN(C_6H_5)_2)Q_2]$	308.0	1506	1.93
$[VO(HCON(CH_3)_2)Q_2]H_2O$	250.4	1216	1.74
$[VO(C_4H_8O_2)Q_2]$	252.0	1129.6	1.66
$[VO(C_4H_8O)Q_2]$	247.0	1172.0	1.695
$[VO(C_4H_4S)Q_2]H_2O$	260.5	1238.0	1.74
$[VO(H_2O)(BzQ)_2]$	269.6	1383.6	1.84
$[VO(H_2O)(nQ)_2]$	232.9	1056.4	1.61
$[VO(OH)Q_2]\,2H_2O$			Diamagnetic
$[VO_2Q(C_5H_5N)]$			"
$[VO_2Q(CH_3.C_5H_4N)]$			"

*Calculated from χ_M (corr.) using the Curie equation $\mu_{eff}=2.84\,(\chi_M\,(corr.)T)^{\frac{1}{2}}$

(BzQH=5:6-Benzoquinaldinic acid, nQH=5-nitroquinaldinic acid).



Picolinic acid, though has the same disposition of the N and COOH, failed to react like quinaldinic acid. Quinolinic acid (pyridine-2,3-dicarboxylic acid), having a molecular weight close to quinaldinic acid, also did not furnish any positive results. Further work with other pyridine and quinoline carboxylic acids is progressing in this laboratory. Investigation are also being carried out on the complexes of $VOCl_3$, VCl_4 and VCl_3 with quinaldinic acid and its derivatives.

**We have just succeeded in isolating some vanadium (III) complexes of quinaldinic acid. This will he reported in due course.

Reference may be made here to the formation of two differently coloured modifications of Fe(II)—quinaldinic acid complex (Rây and Bose, Z. *anal. Chem*, 1933, **95**, 400) as also of cobalt(II)—quinaldinate (Dutt, this *Journal*, 1937, **14**, 572). It is worthwhile therefore to study the reactions of quinaldinic acid with other transition metals. We have already undertaken works in this direction.

EXPERIMENTAL

Quinaldinic acid was prepared from quinaldine (B.D.H.) by following Hammick's procedure (*J. Chem. Soc.*, 1923, **123**, 2882) and was recrystallised twice from hot glacial acetic acid, furnishing light cream-coloured fine needles. Vanadyl sulphate pentahydrate was E. Merck's product. 5-Nitroquinaldinic acid was obtained by nitration of quinaldinic acid (Welcher, "Organic Analytical Reagent", Vol. II, p. 206). 5,6-Benzoquinaldinic acid was prepared according to De (D. Phil. thesis, Calcutta University, 1952).

Oxo-bis quinaldinato-vanadium (IV) *Monohydrate* (*Cream*).—Quinaldinic acid (0.5 g.), dissolved in water (200 c.c.), was treated under stirring with an aqueous solution of vanadyl sulphate (0.25 g. in 10 c.c.). A voluminous cream-coloured precipitate was formed, which was digested on a water bath for half an hour, filtered, washed with water, and dried over $CaCl_2$. {Found: V, 11.58; C, 56.1; H, 3.8; N, 6.57; H_2O (by loss at 110°), 3.80. $[VO(C_{10}H_6O_2N)_2]H_2O$ requires V, 11.88; C, 55.94; H, 3.26; N, 6.53; H_2O, 4.20%}.

Aquo-oxo-bis-quinaldinato-vanadium (IV) (*Olive-green*).—(*a*). An aqueous solution of vanadyl sulphate (0.25 g. in 5 c.c.) was added to a hot methanolic solution of quinaldinic acid (0.5 g. in 40 c.c.), when the cream-coloured compound separated. On keeping the mixture overnight the product turned olive-green. The olive-green crystals were filtered, washed with methanol, and dried over $CaCl_2$. {Found: V, 11.65; C, 56.2; H, 3.6; N, 6.42; H_2O (by loss at 150°), 4.60. $[VO(H_2O)(C_{10}H_6O_2N)_2]$ requires V, 11.88; C, 55.94; H, 3.26; N, 6.53; H_2O, 4.20%}.

(*b*). The oxo-hydroxo-bis-quinaldinato-vanadium(V) was dissolved in methanol (150 c.c), refluxed on a water bath for 15-20 hrs., and then allowed to stand. A crop of olive-green crystals appeared which were treated as above. The mother liquor on further refluxing with methanol produced a fresh crop of the olive-green crystals.

Pyridine-oxo-bis-quinaldinato-vanadium(IV) *Monohydrate*.—The freshly prepared cream-coloured compound was washed with water, sucked dry, and then heated with distilled pyridine (10 c.c.) on the water bath under reflux. The cream-coloured compound readily dissolved producing a greenish solution which soon deposited a fine bluish green crystalline product. After half an hour, the mixture was cooled, the product washed with ethanol first by decantation and then on the filter till free of pyridine, and dried over $CaCl_2$. {Found: V, 9.80; N, 8.46; $(C_5H_5N+H_2O)$, 19.3. $[VO(C_5H_5N)(C_{10}H_6O_2N)_2]$ H_2O requires V, 10.04; N, 8.27; $(C_5H_5N+H_2O)$, 19.1%}.

The same compound was also obtained from the freshly prepared olive-green variety. [Found: V, 9.86; $(C_5H_5N+H_2O)$, 19.1%]. The substance liberates pyridine on heating with NaOH solution.

Pyridine-oxo-bis-quinaldinato-vanadium (IV) was obtained using anhydrous $[VOQ_2]$

and anhydrous pyridine. ⟨ Found: V, 10.70; C_5H_5N(by loss at 130°), 16.70. [$VO(C_5H_5N)$-$(C_{10}H_6O_2N)_2$] requires V, 10.41; C_5H_5N, 16.12% ⟩.

∝-Picoline-oxo-bis-quinaldinato-vanadium (IV).—To quinaldinic acid (0.5 g.), dissolved in ethanol (10. c.c.), was added ∝-picoline (10 c.c.), followed by an aqueous solution of vanadyl sulphate (0.25 g. in 5 c.c.). A clear greenish brown solution was formed, which slowly deposited fine bluish green crystals. These were filtered next day, washed with ethanol, and finally dried over $CaCl_2$. The compound, however, could not be prepared by following the procedure for the pyridine complex. ⟨ Found: V, 10.30; $CH_3.C_5H_4N$, 18.11 (by loss at 130°). [$VO(CH_3.C_5H_4N)(C_{10}H_6O_2N)_2$] requires V, 10.12; $CH_3.C_5H_4N$, 18.45% ⟩.

Aniline-oxo-bis-quinaldinato-vanadium (IV) was obtained as light green microcrystals as in the case of the pyridine complex, using aniline (15 c.c.). ⟨ Found: V, 10.15; N, 8.10; $C_6H_5.NH_2$, 19.0. [$VO(C_6H_5NH_2)(C_{10}H_6O_2N)_2$] requires V, 10.12; N, 8.33; $C_6H_5NH_2$, 18.45% ⟩.

Methylanthranilate-oxo-bis-quinaldinato-vanadium (IV) was prepared like the ∝-picoline compound using methylanthranilate in place of ∝-picoline. The cream-coloured compound, first formed, slowly changed to pale bluish green. After keeping overnight, the crystals were filtered, washed with ethanol and dried over $CaCl_2$. ⟨ Found: V, 9.30; N, 7.20. [$VO(C_6H_4(NH_2)(CO_2Me)(C_{10}H_6O_2N)_2$] requires V, 9.08; N, 7.47% ⟩.

Diphenylamine-oxo-bis-quinaldinato-vanadium (IV).— Quinaldinic acid (0.5 g.) and diphenylamine (5 g.) were heated in ethanol (70 c.c.) on a water bath under reflux. Vanadyl sulphate (0.25 g. in 5 c.c. water) was then added and the mixture refluxed for 2 hours. The cream-coloured precipitate changed to light green. This was then filtered, washed, and dried as usual. ⟨ Found: V, 9.03; N, 7.11. [$VO(HN(Ph)_2(C_{10}H_6O_2N)_2$] requires V, 8.79; N, 7.24% ⟩.

Dimethylformamide-oxo-bis-quinaldinato-vanadium (IV) *monohydrate* was prepared like the pyridine complex using dimethylformamide instead of pyridine. This formed beautiful dark bluish green crystals. ⟨ Found: V, 9.96; N, 8.38; $HCON(CH_3)_2+H_2O$ (by loss at 130°), 18.62. [$VO.(HCONMe_2)(C_{10}H_6O_2N)_2]H_2O$ requires V, 10.16; N, 8.37. ($HCONMe_2$ + H_2O), 18.12% ⟩.

The dioxane and the tetrahydrofuran compounds also were obtained as above.

Dioxan-oxo-bis-quinaldinato-vanadium (IV): ⟨ Found: V, 10.01; $C_4H_8O_2$ (by loss at 130°), 18.1. [$VO(C_4H_8O_2)(C_{10}H_6O_2N)_2$] requires V, 10.22; $C_4H_8O_2$, 17.60% ⟩.

Tetrahydrofuran-oxo-bis-quinaldinato-vanadium (IV): ⟨ Found: V, 10.40; C_4H_8O, 14.74. [$VO(C_4H_8O)(C_{10}H_6O_2N)_2$)] requires V, 10.55; C_4H_8O, 14.96% ⟩.

Thiophen-oxo-bis-quinaldinato-vanadium (IV) *Monohydrate*.—The solution of quinaldinic acid (0.7. g.) in thiophen (10 c.c.) and ethanol (10 c.c.) was heated under reflux (water bath) and treated with the vanadyl sulphate solution (0.5 g. in 5 c.c. water). Immediately a bluish green compound separated; the mixture was refluxed for half an hour, filtered, washed, and dried as usual. ⟨ Found: V, 9.6; ($C_4H_4S+H_2O$), 19.57. [$VO[C_4H_4S)$-$(C_{10}H_6O_2N)_2]H_2O$ requires V, 9.94; ($C_4H_4S+H_2O$), 19.88% ⟩.

Aquo-oxo-bis-5-nitroqunaldinato-vanadium (IV).—To 5-nitroquinaldinic acid (0.5 g.), dissolved in almost boiling water (300 c.c.), vanadyl sulphate (0.2 g. in 10 c.c. water) was

added. A pale apple-green compound was obtained, which was washed with hot water, then with ethanol, and dried over $CaCl_2$. ⟨ Found : V, 9.48; N, 10.96; H_2O(by loss at 150°), 4.3. $[VO(H_2O)(NO_2.C_{10}H_5O_2N)_2]$ requires V, 9.78; N, 10.75; H_2O, 3.4% ⟩.

Aquo-oxo-bis-5,6-benzoquinaldinato-vanadium (IV).—To 5,6-benzoquinaldinic acid (0.6 g.), dissolved in ethanol (50 c.c.), was added $VOSO_4.5H_2O$ (0.25 g. in 5 c.c. water). A deep cream-coloured compound separated which was filtered, washed with ethanol, and dried over $CaCl_2$. ⟨ Found: V, 9.23; N, 5.26; H_2O (by loss at 150°), 3.5. $[VO(H_2O)(C_{14}H_{14}O_2N)_2]$ requires V, 9.56; N, 5.26; H_2O, 3.37% ⟩. The vanadium (IV) complex could not be prepared in aqueous medium only due to the extreme insolubility of the reagent.

Oxo-hydroxo-bis quinaldinato-vanadium (V) *Dihydrate*.—Ammonium vanadate (0.2g. in 15c.c. water) was added to quinaldinic acid (1 g. in 150 c.c. water) when a yellowish white precipitate separated. It was digested on a water bath for half an hour, filtered, and finally recrystallised from hot ethanol. ⟨ Found: V, 10.85; N, 6.03; H_2O, 7.20. $[VO(OH)(C_{10}H_6O_2N)_2]$ $2H_2O$ requires V, 10.99; N, 6.03; H_2O, 7.75% ⟩.

Pyridine-dioxo-monoquinaldinato-vanadium (V).—The compound, oxo-hydroxo-bis-quinaldinato-vanadium (V) was prepared, as described before, and was then treated with pyridine (7-8 c.c.). The mixture was warmed on a water bath for half an hour, when a clear solution was obtained. This, on cooling in ice, furnished colorless crystals which were filtered, washed with ice-cold water, and dried as usual. ⟨ Found: V, 15.01; N, 8.44. C_5H_5N (by loss at 170°), 23.25. $[VO_2(C_5H_5N)(C_{10}H_6O_2N)]$ requires V, 15.26; N, 8.38; C_5H_5N, 23.65%. Found: V, 19.54; N, 5.91. $[VO_2(C_{10}H_6O_2N)]$ requires V, 20.00, N, 5.49% ⟩.

α-Picoline-dioxo-monoquinaldinato-vanadium (V) was obtained as above using α-picolinde in place of pyridine. ⟨ Found: V, 14.63; N, 7.99; $CH_3C_5H_4N$(by loss at 210°), 26.79. $[VO_2(CH_3C_5H_4N)(C_{10}H_{14}N)$ requires V, 14.63; N, 8.04; $CH_3C_5H_6O_2N$, 26.72% ⟩. Found: V, 20.00; N, 6.01 $[VO_2(C_{10}H_6O_2N)]$ requires V, 20.00, N, 5.49% ⟩.

Analytical Methods.—Vanadium content was determined either by decomposing the complex with HNO_3 and H_2SO_4 and then igniting to V_2O_5 or by igniting the complex under a thick layer of oxalic acid to the V_2O_5 stage. Nitrogen was estimated by combustion technique.

X-ray Measurement.—X-ray powder photographs were taken with Phillips PW 1010 X-ray unit with Phillips Debye-Scherrer camera with 57.3 mm diameter using CuK_α radiation.

Magnetic Measurements.—The magnetic moments were determined by the Gouy method using a semi micro Mettler balance for measuring the difference in weight and with a field strength of 9.26 gauss. Diamagnetic corrections were taken from Selwood "Magnetochemistry", Interscience, New York, p. 78, 1956).

The infrared spectra were scanned on a Perkin-Elmer 21 Infrared Spectrometer using KBr disc technique.

The pyrolysis curves (Fig. 4 and Fig. 5) were recorded in a Chevenard thermobalance (approximate rate of heating, 5° per minute).

The authors acknowledge their indebtedness to Prof. P. Rây and to Dr. P. C. Banerjee for criticism and suggestions, to Prof. A. K. Majumdar and Sri Bidhan Chandra Bhattacharya of Jadavpur University for the pyrolysis curves (Fig. 4 and 5), to Dr. Supriya Roy of the same University for the microphotograph, to Dr. J. N. Chatterjea of Science College, Patna, for the analyses of carbon and hydrogen, to Dr. Ranjit Sengupta and Sri P. Srivastava of this Institute for the X-ray studies, and to Dr. N. K. Dutt and Sri N. N. Ghosh of the University College of Sciences and Technology, Calcutta, for permitting them the use of the Gouy magnetic balance. They also gratefully acknowledge the services of Sadtler Research Laboratories, Philadelphia, U. S. A., for the infra-red spectrograms. They are also indebted to Dr. K. Banerjee, Director of this Institute, for kindly permitting them to continue as guest workers as also for his keen interest in this work.

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Received May 30, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 12, 1961]

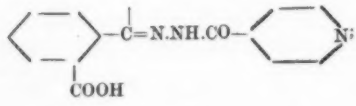
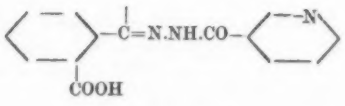
Fungicidal and Bactericidal Studies of Some Hydrazones. Part I

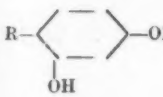
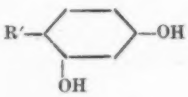
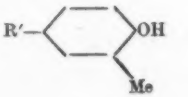
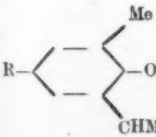
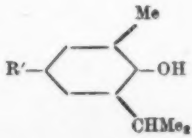
(Miss) Kanti Srivastava and J. K. Mehrotra

Several substituted benzophenone nicotinyl- and isonicotinyl-hydrazones have been prepared and tested for their activities on *Aspergillus niger* and *S. aureus*.

In the present investigation several substituted benzoylbenzoic acids have been prepared by the decomposition of phenolphthaleins through oxime formation (Hubacher, *J. Amer. Chem. Soc.*, 1946, **68**, 718) and fluoresceins by alkali fusion (Baeyer, *Annalen*, 1876, **23**, 183). The acids thus obtained have been condensed with isonicotinic and nicotinic acid hydrazides. The hydrazones thus produced have been tested for their fungicidal activity on *Aspergillus niger* and bacteriostatic activity on *S. aureus* by tube dilution method. The minimum concentrations of these for complete inhibition in 2 c.c. of the medium are shown in Table I.

TABLE I

R =  R′= 

Compound.	Conc. for complete inhibition of *A. niger.*	Conc. for complete inhibition of *S. aureus.*	Compound.	Conc. for complete inhibition of *A. niger.*	Conc. for complete inhibition of *S. aureus.*
	12.500 mg.	1.562 mg.		Nil	1.562 mg,
	3.125	0.781		6.250 mg.	0.781
	Nil	1.562		1.562	1.562
	3.125	1.562		6.250	3.125

Insonicotinic and nicotinic acid hydrazides are known to possess little or no fungicidal properties (F. W. Bieberdorf, "Antibiotic and Chemotheraphy", 1953, vol. **3**, pp. 513-20).

The present investigation indicates that their hydrazones with substituted benzoylbenz ic acids show some fungicidal properties. As expected, these hydrozones also possess bactericidal properties.

EXPERIMENTAL

4-Hydroxy-2′-carboxybenzophenone Isonicotinylhydrazone.—2-(4-Hydroxy)benzoylbenzoic acid (2.42 g.) was refluxed for 3 hours with isonicotinic acid hydrazide (1.37 g.) in ethanol (10 c.c.). After cooling, the crystals were filtered, washed with a little cold ethanol, and recrystallised from 60-80% ethanol when light yellow crystals of the hydrazone, m.p. 145°, was obtained in 60% yield. (Found: N, 11.46. $C_{20}H_{15}O_4N_3$ requires N, 11.63%). It develops a violet colour with aqueous NaOH and effervesces with $NaHCO_3$. Other benzophenone isonicotinylhydrazones, prepared in the same way, are recorded in Table II. All the compounds effervesce with $NaHCO_3$.

TABLE II

2′-Carboxybenzophenone isonicotinyhyldrazones.

Isonicotinic acid hydrazide taken = 1.37g.

Compound.	Benzoylbenzoic acid.	Colour.	Yield.	M.P.	Formula.	%Nitrogen. Found.	%Nitrogen. Calc.	Colour with NaOH.
2,4-Dihydroxy-	2-(2,4-Dihydroxy)-(2.58g.).	Dirty white	66%	170°	$C_{20}H_{15}O_5N_3$	11.38	11.14	Light yellow
3-Methyl-4-hydroxy-	2-(3-Methyl-4-hydroxy)-(2.56g.)	Pinkish white	45	150°	$C_{21}H_{17}O_4N_3$	11.63	11.20	Violet
2-Methyl-4-hydroxy-5-propyl-	2-(2-Methyl-4-hydroxy-5-propyl-)-(2.98g.)	Chocolate needles	50	173°	$C_{24}H_{23}O_4N_3$	10.12	10.07	Blue

4-Hydroxy-2′-carboxybenzophenone Nicotinylhydrazone.—2-(4-Hydroxy)benzoylbenzoic acid (2.42 g.) and nicotinic acid hydrazide (1.37 g.) gave pinkish white crystals in 68% yield, m.p. 140°. (Found N, 11.44. $C_{20}H_{15}O_4N_3$ requires N, 11.63%). It develops a violet colour with NaOH and effervesces with $NaHCO_3$. Other benzophenone derivatives prepared from nicotinic acid hydrazide (1.37 g.) are recorded in Table III. All the products effervesce with $NaHCO_3$.

TABLE III

2′-Carboxybenzophenone nicotinylhydrazones.

Compound.	Benzoylbenzoic acid.	Colour.	Yield.	M.P.	Formula.	%Nitrogen. Found.	%Nitrogen. Calc.	Colour with NaOH.
2,4-Dihyroxy-	2-(2,4-Dihydroxy)-(2.58 g.)	Yellow	45%	160°	$C_{20}H_{15}O_5N_3$	11.29	11.14	Yellow
3-Methyl-4-hydroxy-	2-(3-Methyl-4-hydroxy)-(2.56 g.)	Pink	37	140°	$C_{21}H_{17}O_4N_3$	11.06	11.20	Violet
2-Methyl-4-hydroxy-5-propyl-	2-(2-Methyl-4-hydroxy-5-propyl-)-(2.98 g.)	White	48	160°	$C_{24}H_{23}O_4N_3$	10.36	10.07	Yellow

Fungicidal and Bacteriostatic Studies

For testing of fungicidal activities of the compounds, potato—glucose medium was used and for the testing of bacterial activity nutrient broth medium containing beef extract and peptone was used. *Aspergillus niger* and *S. aureus* respectively were used for this purpose; 2 c.c. of the medium was taken in each of the ten tubes. To the first tube 2 c.c. of a solution of a compound containing 0.0625 g./10 c.c. was added; 2 c.c. of this mixture was withdrawn and added to the second tube and the process continued to 9th tube. The tenth tube contained only the medium. The tubes were inoculated with a 24 hours' grown culture. The concentrations at which there was complete inhibition was recorded.

The authors wish to express their thanks to Dr. S. D. Verma for his keen interest and help.

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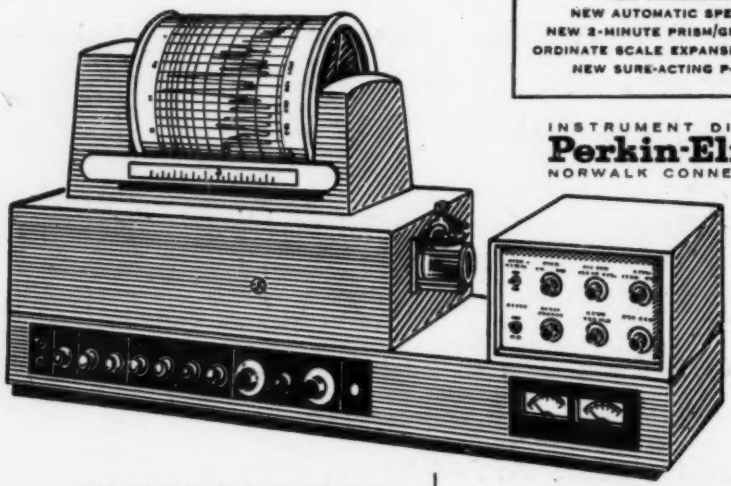

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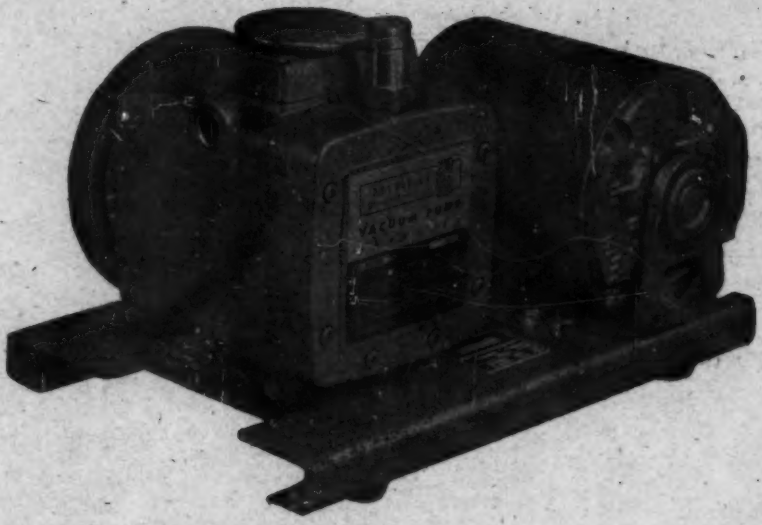

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Printed & Published by G. Banerjee, M.Sc., Asst. Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-9, at Inland Printing Works, 60-3 Dharamtala Street, Calcutta-13.